

6.3.6 Regulators. For required gas cylinders.

6.3.7 Headspace Vial Pre-Pressurizer. Nitrogen pressurized hypodermic needle inside protective shield.

7.0 Reagents and Standards

7.1 Analysis. Same as Method 106, Section 7.1, with the addition of the following:

7.1.1 Water. Interference-free.

7.2 Calibration. The following items are required for calibration:

7.2.1 Cylinder Standards (4). Gas mixture standards (50-, 500-, 2000- and 4000-ppm vinyl chloride in nitrogen cylinders). Cylinder standards may be used directly to prepare a chromatograph calibration curve as described in Section 10.3, if the following conditions are met: (a) The manufacturer certifies the gas composition with an accuracy of ± 3 percent or better (see Section 7.2.1.1). (b) The manufacturer recommends a maximum shelf life over which the gas concentration does not change by greater than ± 5 percent from the certified value. (c) The manufacturer affixes the date of gas cylinder preparation, certified vinyl chloride concentration, and recommended maximum shelf life to the cylinder before shipment to the buyer.

7.2.1.1 Cylinder Standards Certification. The manufacturer shall certify the concentration of vinyl chloride in nitrogen in each cylinder by (a) directly analyzing each cylinder and

(b) calibrating the analytical procedure on the day of cylinder analysis. To calibrate the analytical procedure, the manufacturer shall use, as a minimum, a 3-point calibration curve. It is recommended that the manufacturer maintain (1) a high-concentration calibration standard (between 4000 and 8000 ppm) to prepare the calibration curve by an appropriate dilution technique and (2) a low-concentration calibration standard (between 50 and 500 ppm) to verify the dilution technique used. If the difference between the apparent concentration read from the calibration curve and the true concentration assigned to the low-concentration calibration standard exceeds 5 percent of the true concentration, the manufacturer shall determine the source of error and correct it, then repeat the 3-point calibration.

7.2.1.2 Verification of Manufacturer's Calibration Standards. Before using, the manufacturer shall verify each calibration standard by (a) comparing it to gas mixtures prepared (with 99 mole percent vinyl chloride) in accordance with the procedure described in Section 10.1 of Method 106 or by (b) calibrating it against vinyl chloride cylinder Standard Reference Materials (SRMs) prepared by the National Institute of Standards and Technology, if such SRMs are available. The agreement between the initially determined concentration value and the verification concentration value must be

within 5 percent. The manufacturer must reverify all calibration standards on a time interval consistent with the shelf life of the cylinder standards sold.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Sample Collection.

8.1.1 PVC Sampling. Allow the resin or slurry to flow from a tap on the tank or silo until the tap line has been well purged. Extend and fill a 60-ml sample bottle under the tap, and immediately tighten a cap on the bottle. Wrap adhesive tape around the cap and bottle to prevent the cap from loosening. Place an identifying label on each bottle, and record the date, time, and sample location both on the bottles and in a log book.

8.1.2 Water Sampling. At the sampling location fill the vials bubble-free to overflowing so that a convex meniscus forms at the top. The excess water is displaced as the sealing disc is carefully placed, with the Teflon side down, on the opening of the vial. Place the aluminum seal over the disc and the neck of the vial, and crimp into place. Affix an identifying label on the bottle, and record the date, time, and sample location both on the vials and in a log book.

8.2 Sample Storage. All samples must be analyzed within 24 hours of collection, and must be refrigerated during this period.

9.0 Quality Control

Section	Quality control measure	Effect
10.3	Chromatograph calibration	Ensure precision and accuracy of chromatograph.

10.0 Calibration and Standardization

Note: Maintain a laboratory log of all calibrations.

10.1 Preparation of Standards. Calibration standards are prepared as follows: Place 100 μ l or about two equal drops of distilled water in the sample vial, then fill the vial with the VCM/nitrogen standard, rapidly seat the septum, and seal with the aluminum cap. Use a $\frac{1}{8}$ -in. stainless steel line from the cylinder to the vial. Do not use rubber or Tygon tubing. The sample line from the cylinder must be purged (into a properly vented hood) for several minutes prior to filling the vials. After purging, reduce the flow rate to between 500 and 1000 cc/min. Place end of tubing into vial (near bottom). Position a septum on top of the vial, pressing it against the $\frac{1}{8}$ -in. filling tube to minimize the size of the vent opening.

This is necessary to minimize mixing air with the standard in the vial. Each vial is to be purged with standard for 90 seconds, during which time the filling tube is gradually slid to the top of the vial. After the 90 seconds, the tube is removed with the septum, simultaneously sealing the vial. Practice will be necessary to develop good technique. Rubber gloves should be worn during the above operations. The sealed vial must then be pressurized for 60 seconds using the vial prepressurizer. Test the vial for leakage by placing a drop of water on the septum at the needle hole. Prepressurization of standards is not required unless samples have been prepressurized.

10.2 Analyzer Calibration. Calibration is to be performed each 8-hour period the chromatograph is used. Alternatively, calibration with duplicate

50-, 500-, 2,000-, and 4,000-ppm standards (hereafter described as a four-point calibration) may be performed on a monthly basis, provided that a calibration confirmation test consisting of duplicate analyses of an appropriate standard is performed once per plant shift, or once per chromatograph carousel operation (if the chromatograph operation is less frequent than once per shift). The criterion for acceptance of each calibration confirmation test is that both analyses of 500-ppm standards [2,000-ppm standards if dispersion resin (excluding latex resin) samples are being analyzed] must be within 5 percent of the most recent four-point calibration curve. If this criterion is not met, then a complete four-point calibration must be performed before sample analyses can proceed.

10.3 Preparation of Chromatograph Calibration Curve. Prepare two vials each of 50-, 500-, 2,000-, and 4,000-ppm standards. Run the calibration samples in exactly the same manner as regular samples. Plot A_s , the integrator area counts for each standard sample, versus C_c , the concentration of vinyl chloride in each standard sample. Draw a straight line through the points derived by the least squares method.

11.0 Analytical Procedure

11.1 Preparation of Equipment. Install the chromatographic column and

condition overnight at 160 °C (320 °F). In the first operation, Porapak columns must be purged for 1 hour at 230 °C (450 °F).

Do not connect the exit end of the column to the detector while conditioning. Hydrogen and air to the detector must be turned off while the column is disconnected.

11.2 Flow Rate Adjustments. Adjust flow rates as follows:

11.2.1. Nitrogen Carrier Gas. Set regulator on cylinder to read 50 psig. Set regulator on chromatograph to produce a flow rate of 30.0 cc/min. Accurately

measure the flow rate at the exit end of the column using the soap film flowmeter and a stopwatch, with the oven and column at the analysis temperature. After the instrument program advances to the "B" (backflush) mode, adjust the nitrogen pressure regulator to exactly balance the nitrogen flow rate at the detector as was obtained in the "A" mode.

11.2.2. Vial Prepressurizer Nitrogen.

11.2.2.1 After the nitrogen carrier is set, solve the following equation and adjust the pressure on the vial prepressurizer accordingly.

$$P = \frac{T_1}{T_2} \left[P_1 - \frac{P_{w1} - P_{w2}}{7.50} \right] - 10 \text{ kPa} \quad \text{Eq. 107-1}$$

Where:

T_1 = Ambient temperature, °K (°R).

T_2 = Conditioning bath temperature, °K (°R).

P_1 = Gas chromatograph absolute dosing pressure (analysis mode), k Pa.

P_{w1} = Water vapor pressure 525.8 mm Hg @ 90 °C.

P_{w2} = Water vapor pressure 19.8 mm Hg @ 22 °C.

7.50 = mm Hg per k Pa.

10 kPa = Factor to adjust the prepressurized pressure to slightly less than the dosing pressure.

11.2.2.2 Because of gauge errors, the apparatus may over-pressurize the vial. If the vial pressure is at or higher than the dosing pressure, an audible double injection will occur. If the vial pressure is too low, errors will occur on resin samples because of inadequate time for head-space gas equilibrium. This condition can be avoided by running several standard gas samples at various pressures around the calculated pressure, and then selecting the highest pressure that does not produce a double injection. All samples and standards must be pressurized for 60 seconds using the vial prepressurizer. The vial is then placed into the 90 °C conditioning bath and tested for leakage by placing a drop of water on the septum at the needle hole. A clean, burr-free needle is mandatory.

11.2.3. Burner Air Supply. Set regulator on cylinder to read 50 psig. Set regulator on chromatograph to supply air to burner at a rate between 250 and 300 cc/min. Check with bubble flowmeter.

11.2.4. Hydrogen Supply. Set regulator on cylinder to read 30 psig. Set regulator on chromatograph to supply approximately 35 ± 5 cc/min. Optimize hydrogen flow to yield the most sensitive detector response without

extinguishing the flame. Check flow with bubble meter and record this flow.

11.3 Temperature Adjustments. Set temperatures as follows:

11.3.1. Oven (chromatograph column), 140 °C (280 °F).

11.3.2. Dosing Line, 150 °C (300 °F).

11.3.3. Injection Block, 170 °C (340 °F).

11.3.4. Sample Chamber, Water Temperature, 90 °C ± 1.0 °C (194 °F ± 1.8 °F).

11.4 Ignition of Flame Ionization Detector. Ignite the detector according to the manufacturer's instructions.

11.5 Amplifier Balance. Balance the amplifier according to the manufacturer's instructions.

11.6 Programming the Chromatograph. Program the chromatograph as follows:

11.6.1. I — Dosing or Injection Time. The normal setting is 2 seconds.

11.6.2. A — Analysis Time. The normal setting is approximately 70 percent of the VCM retention time. When this timer terminates, the programmer initiates backflushing of the first column.

11.6.3. B — Backflushing Time. The normal setting is double the analysis time.

11.6.4. W — Stabilization Time. The normal setting is 0.5 min to 1.0 min.

11.6.5. X — Number of Analyses Per Sample. The normal setting is one.

11.7. Sample Treatment. All samples must be recovered and analyzed within 24 hours after collection.

11.7.1 Resin Samples. The weight of the resin used must be between 0.1 and 4.5 grams. An exact weight must be obtained (within ±1 percent) for each sample. In the case of suspension resins, a volumetric cup can be prepared for holding the required amount of sample. When the cup is used, open the sample

bottle, and add the cup volume of resin to the tared sample vial (tared, including septum and aluminum cap). Obtain the exact sample weight, add 100 ml or about two equal drops of water, and immediately seal the vial. Report this value on the data sheet; it is required for calculation of RVC. In the case of dispersion resins, the cup cannot be used. Weigh the sample in an aluminum dish, transfer the sample to the tared vial, and accurately weigh it in the vial. After prepressurization of the samples, condition them for a minimum of 1 hour in the 90 °C (190 °F) bath. Do not exceed 5 hours. Prepressurization is not required if the sample weight, as analyzed, does not exceed 0.2 gram. It is also not required if solution of the prepressurization equation yields an absolute prepressurization value that is within 30 percent of the atmospheric pressure.

Note: Some aluminum vial caps have a center section that must be removed prior to placing into sample tray. If the cap is not removed, the injection needle will be damaged.

11.7.2 Suspension Resin Slurry and Wet Cake Samples. Decant the water from a wet cake sample, and turn the sample bottle upside down onto a paper towel. Wait for the water to drain, place approximately 0.2 to 4.0 grams of the wet cake sample in a tared vial (tared, including septum and aluminum cap) and seal immediately. Then determine the sample weight (1 percent). All samples weighing over 0.2 gram, must be prepressurized prior to conditioning for 1 hour at 90 °C (190 °F), except as noted in Section 11.7.1. A sample of wet cake is used to determine total solids (TS). This is required for calculating the RVC.

11.7.3 Dispersion Resin Slurry and Geon Latex Samples. The materials

should not be filtered. Sample must be thoroughly mixed. Using a tared vial (tared, including septum and aluminum cap) add approximately eight drops (0.25 to 0.35 g) of slurry or latex using a medicine dropper. This should be done immediately after mixing. Seal the vial as soon as possible. Determine sample weight (1 percent). Condition the vial for 1 hour at 90 °C (190 °F) in the analyzer bath. Determine the TS on the slurry sample (Section 11.10).

11.7.4 In-process Wastewater Samples. Using a tared vial (tared, including septum and aluminum cap) quickly add approximately 1 cc of water using a medicine dropper. Seal the vial as soon as possible. Determine sample weight (1 percent). Condition the vial for 1 hour at 90 °C (190 °F) in the analyzer bath.

11.8 Preparation of Sample Turntable.

11.8.1 Before placing any sample into turntable, be certain that the center section of the aluminum cap has been removed. The numbered sample vials should be placed in the corresponding numbered positions in the turntable. Insert samples in the following order:

11.8.1.1 Positions 1 and 2. Old 2000-ppm standards for conditioning. These are necessary only after the analyzer has not been used for 24 hours or longer.

11.8.1.2 Position 3. 50-ppm standard, freshly prepared.

11.8.1.3 Position 4. 500-ppm standard, freshly prepared.

11.8.1.4 Position 5. 2000-ppm standard, freshly prepared.

11.8.1.5 Position 6. 4000-ppm standard, freshly prepared.

11.8.1.6 Position 7. Sample No. 7 (This is the first sample of the day, but is given as 7 to be consistent with the turntable and the integrator printout.)

11.8.2 After all samples have been positioned, insert the second set of 50-, 500-, 2000-, and 4000-ppm standards. Samples, including standards, must be conditioned in the bath of 90 °C (190 °F) for a minimum of one hour and a maximum of five hours.

11.9 Start Chromatograph Program. When all samples, including standards, have been conditioned at 90 °C (190 °F) for at least one hour, start the analysis program according to the manufacturer's instructions. These instructions must be carefully followed when starting and stopping a program to prevent damage to the dosing assembly.

11.10 Determination of Total Solids. For wet cake, slurry, resin solution, and PVC latex samples, determine TS for each sample by accurately weighing approximately 3 to 4 grams of sample in an aluminum pan before and after placing in a draft oven (105 to 110 °C (221 to 230 °F)). Samples must be dried to constant weight. After first weighing,

return the pan to the oven for a short period of time, and then reweigh to verify complete dryness. The TS are then calculated as the final sample weight divided by initial sample weight.

12.0 Calculations and Data Analysis

12.1 Nomenclature.

A_s = Chromatogram area counts of vinyl chloride for the sample, area counts.

A_s = Chromatogram area counts of vinyl chloride for the sample.

C_c = Concentration of vinyl chloride in the standard sample, ppm.

K_p = Henry's Law Constant for VCM in PVC 90 °C, 6.52×10^{-6} g/g/mm Hg.

K_w = Henry's Law Constant for VCM in water 90 °C, 7×10^{-7} g/g/mm Hg.

M_v = Molecular weight of VCM, 62.5 g/mole.

m = Sample weight, g.

P_a = Ambient atmospheric pressure, mm Hg.

R = Gas constant, (62360 ³ ml) (mm Hg)/(mole)(°K).

R_f = Response factor in area counts per ppm VCM.

R_s = Response factor, area counts/ppm.

T_1 = Ambient laboratory temperature, °K.

TS = Total solids expressed as a decimal fraction.

T_2 = Equilibrium temperature, °K.

V_g = Volume of vapor phase, ml.

$$= V_v - \frac{m(TS)}{1.36} - \frac{m(1-TS)}{0.9653}$$

V_v = Vial volume, ³ ml.

1.36 = Density of PVC at 90 °C, g/³ ml.

0.9653 = Density of water at 90 °C, g/³ ml.

12.2 Response Factor. If the calibration curve described in Section 10.3 passes through zero, an average response factor, R_f , may be used to

facilitate computation of vinyl chloride sample concentrations.

12.2.1 To compute R_f , first compute a response factor, R_s , for each sample as follows:

$$R_s = \frac{A_s}{C_c} \quad \text{Eq. 107-2}$$

12.2.2 Sum the individual response factors, and calculate R_f . If the calibration curve does not pass through

zero, use the calibration curve to determine each sample concentration.

12.3 Residual Vinyl Chloride Monomer Concentration, (C_{rvc}) or Vinyl

Chloride Monomer Concentration. Calculate C_{rvc} in ppm or mg/kg as follows:

$$C_{rvc} = \frac{A_s P_a}{R_f T_1} \left[\frac{M_v V_g}{R m} + K_p (TS) T_2 K_w (1-TS) T_2 \right] \quad \text{Eq. 107-3}$$

Note: Results calculated using these equations represent concentration based on the total sample. To obtain results based on dry PVC content, divide by TS.

13.0 Method Performance

13.1 Range and Sensitivity. The lower limit of detection of vinyl chloride will vary according to the

sampling and chromatographic system. The system should be capable of producing a measurement for a 50-ppm vinyl chloride standard that is at least

10 times the standard deviation of the system background noise level.

13.2 An interlaboratory comparison between seven laboratories of three resin samples, each split into three parts, yielded a standard deviation of 2.63 percent for a sample with a mean of 2.09 ppm, 4.16 percent for a sample with a mean of 1.66 ppm, and 5.29 percent for a sample with a mean of 62.66 ppm.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. B.F. Goodrich, Residual Vinyl Chloride Monomer Content of Polyvinyl Chloride Resins, Latex, Wet Cake, Slurry and Water Samples. B.F. Goodrich Chemical Group

Standard Test Procedure No. 1005-E. B.F. Goodrich Technical Center, Avon Lake, Ohio. October 8, 1979.

2. Berens, A.R. The Diffusion of Vinyl Chloride in Polyvinyl Chloride. ACS-Division of Polymer Chemistry, Polymer Preprints 15 (2):197. 1974.

3. Berens, A.R. The Diffusion of Vinyl Chloride in Polyvinyl Chloride. ACS-Division of Polymer Chemistry, Polymer Preprints 15 (2):203. 1974.

4. Berens, A.R., *et al.* Analysis for Vinyl Chloride in PVC Powders by Head-Space Gas Chromatography. Journal of Applied Polymer Science. 19:3169-3172. 1975.

5. Mansfield, R.A. The Evaluation of Henry's Law Constant (Kp) and Water Enhancement in the Perkin-Elmer Multifract F-40 Gas Chromatograph. B.F. Goodrich. Avon Lake, Ohio. February 10, 1978.

17.0 Tables, Diagrams, Flowcharts, and Validation Data [Reserved]

Method 108—Determination of Particulate and Gaseous Arsenic Emissions

Note: This method does not include all of the specifications (e.g., equipment and supplies) and procedures (e.g., sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in Appendix A to 40 CFR Part 60. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 2, Method 3, Method 5, and Method 12.

1.0 Scope and Application.

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Arsenic compounds as arsenic (As)	7440-38-2	Lower limit 10 µg/ml or less.

1.2 Applicability. This method is applicable for the determination of inorganic As emissions from stationary sources as specified in an applicable subpart of the regulations.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

Particulate and gaseous As emissions are withdrawn isokinetically from the source and are collected on a glass mat filter and in water. The collected arsenic is then analyzed by means of atomic absorption spectrophotometry (AAS).

3.0 Definitions. [Reserved]

4.0 Interferences

Analysis for As by flame AAS is sensitive to the chemical composition and to the physical properties (e.g., viscosity, pH) of the sample. The analytical procedure includes a check for matrix effects (Section 11.5).

5.0 Safety

5.1 This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive reagents. The following reagents are hazardous. Personal protective equipment and safe procedures that prevent chemical

splashes are recommended. If contact occurs, immediately flush with copious amounts of water for at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burns as thermal burns.

5.2.1 Hydrochloric Acid (HCl). Highly corrosive liquid with toxic vapors. Vapors are highly irritating to eyes, skin, nose, and lungs, causing severe damage. May cause bronchitis, pneumonia, or edema of lungs. Exposure to concentrations of 0.13 to 0.2 percent can be lethal to humans in a few minutes. Provide ventilation to limit exposure. Reacts with metals, producing hydrogen gas.

5.2.2 Hydrogen Peroxide (H₂O₂). Very harmful to eyes. 30% H₂O₂ can burn skin, nose, and lungs.

5.2.3 Nitric Acid (HNO₃). Highly corrosive to eyes, skin, nose, and lungs. Vapors are highly toxic and can cause bronchitis, pneumonia, or edema of lungs. Reaction to inhalation may be delayed as long as 30 hours and still be fatal. Provide ventilation to limit exposure. Strong oxidizer. Hazardous reaction may occur with organic materials such as solvents.

5.2.4 Sodium Hydroxide (NaOH). Causes severe damage to eyes and skin. Inhalation causes irritation to nose, throat, and lungs. Reacts exothermically with small amounts of water.

6.0 Equipment and Supplies

6.1 Sample Collection. A schematic of the sampling train used in performing this method is shown in Figure 108-1; it is similar to the Method 5 sampling train of 40 CFR Part 60, Appendix A.

The following items are required for sample collection:

6.1.1 Probe Nozzle, Probe Liner, Pitot Tube, Differential Pressure Gauge, Filter Holder, Filter Heating System, Temperature Sensor, Metering System, Barometer, and Gas Density Determination Equipment. Same as Method 5, Sections 6.1.1.1 to 6.1.1.7, 6.1.1.9, 6.1.2, and 6.1.3, respectively.

6.1.2 Impingers. Four impingers connected in series with leak-free ground-glass fittings or any similar leak-free noncontaminating fittings. For the first, third, and fourth impingers, use the Greenburg-Smith design, modified by replacing the tip with a 1.3-cm ID (0.5-in.) glass tube extending to about 1.3 cm (0.5 in.) from the bottom of the flask. For the second impinger, use the Greenburg-Smith design with the standard tip. Modifications (e.g., flexible connections between the impingers, materials other than glass, or flexible vacuum lines to connect the filter holder to the condenser) are subject to the approval of the Administrator.

6.1.3 Temperature Sensor. Place a temperature sensor, capable of measuring temperature to within 1 °C (2 °F), at the outlet of the fourth impinger for monitoring purposes.

6.2 Sample Recovery. The following items are required for sample recovery:

6.2.1 Probe-Liner and Probe-Nozzle Brushes, Petri Dishes, Graduated Cylinder and/or Balance, Plastic Storage Containers, and Funnel and Rubber Policeman. Same as Method 5, Sections 6.2.1 and 6.2.4 to 6.2.8, respectively.

6.2.2 Wash Bottles. Polyethylene (2).

6.2.3 Sample Storage Containers. Chemically resistant, polyethylene or

polypropylene for glassware washes, 500- or 1000-ml.

6.3 Analysis. The following items are required for analysis:

6.3.1 Spectrophotometer. Equipped with an electrodeless discharge lamp and a background corrector to measure absorbance at 193.7 nanometers (nm). For measuring samples having less than 10 µg As/ml, use a vapor generator accessory or a graphite furnace.

6.3.2 Recorder. To match the output of the spectrophotometer.

6.3.3 Beakers. 150 ml.

6.3.4 Volumetric Flasks. Glass 50-, 100-, 200-, 500-, and 1000-ml; and polypropylene, 50-ml.

6.3.5 Balance. To measure within 0.5 g.

6.3.6 Volumetric Pipets. 1-, 2-, 3-, 5-, 8-, and 10-ml.

6.3.7 Oven.

6.3.8 Hot Plate.

7.0 Reagents and Standards

Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available; otherwise, use the best available grade.

7.1 The following reagents are required for sample collection:

7.1.1 Filters. Same as Method 5, Section 7.1.1, except that the filters need not be unreactive to SO₂.

7.1.2 Silica Gel, Crushed Ice, and Stopcock Grease. Same as Method 5, Sections 7.1.2, 7.1.4, and 7.1.5, respectively.

7.1.3 Water. Deionized distilled to meet ASTM D 1193-77 or 91 (incorporated by reference-see § 61.18), Type 3. When high concentrations of organic matter are not expected to be present, the KMnO₄ test for oxidizable organic matter may be omitted.

7.2 Sample Recovery.

7.2.1 0.1 N NaOH. Dissolve 4.00 g of NaOH in about 500 ml of water in a 1-liter volumetric flask. Then, dilute to exactly 1.0 liter with water.

7.3 Analysis. The following reagents and standards are required for analysis:

7.3.1 Water. Same as Section 7.1.3.

7.3.2 Sodium Hydroxide, 0.1 N. Same as in Section 7.2.1.

7.3.3 Sodium Borohydride (NaBH₄), 5 Percent Weight by Volume (W/V). Dissolve 50.0 g of NaBH₄ in about 500 ml of 0.1 N NaOH in a 1-liter volumetric flask. Then, dilute to exactly 1.0 liter with 0.1 N NaOH.

7.3.4 Hydrochloric Acid, Concentrated.

7.3.5 Potassium Iodide (KI), 30 Percent (W/V). Dissolve 300 g of KI in 500 ml of water in a 1 liter volumetric

flask. Then, dilute to exactly 1.0 liter with water.

7.3.6 Nitric Acid, Concentrated.

7.3.7 Nitric Acid, 0.8 N. Dilute 52 ml of concentrated HNO₃ to exactly 1.0 liter with water.

7.3.8 Nitric Acid, 50 Percent by Volume (V/V). Add 50 ml concentrated HNO₃ to 50 ml water.

7.3.9 Stock Arsenic Standard, 1 mg As/ml. Dissolve 1.3203 g of primary standard grade As₂O₃ in 20 ml of 0.1 N NaOH in a 150 ml beaker. Slowly add 30 ml of concentrated HNO₃. Heat the resulting solution and evaporate just to dryness. Transfer the residue quantitatively to a 1-liter volumetric flask, and dilute to 1.0 liter with water.

7.3.10 Arsenic Working Solution, 1.0 µg As/ml. Pipet exactly 1.0 ml of stock arsenic standard into an acid-cleaned, appropriately labeled 1-liter volumetric flask containing about 500 ml of water and 5 ml of concentrated HNO₃. Dilute to exactly 1.0 liter with water.

7.3.11 Air. Suitable quality for AAS analysis.

7.3.12 Acetylene. Suitable quality for AAS analysis.

7.3.13 Nickel Nitrate, 5 Percent Ni (W/V). Dissolve 24.780 g of nickel nitrate hexahydrate [Ni(NO₃)₂·6H₂O] in water in a 100-ml volumetric flask, and dilute to 100 ml with water.

7.3.14 Nickel Nitrate, 1 Percent Ni (W/V). Pipet 20 ml of 5 percent nickel nitrate solution into a 100-ml volumetric flask, and dilute to exactly 100 ml with water.

7.3.15 Hydrogen Peroxide, 3 Percent by Volume. Pipet 50 ml of 30 percent H₂O₂ into a 500-ml volumetric flask, and dilute to exactly 500 ml with water.

7.3.16 Quality Assurance Audit Samples. When making compliance determinations, and upon availability, audit samples may be obtained from the appropriate EPA regional Office or from the responsible enforcement authority.

Note: The responsible enforcement authority should be notified at least 30 days prior to the test date to allow sufficient time for sample delivery.

8.0 Sample Collection, Preservation, Transport, and Storage

8.1 Pretest Preparation. Follow the general procedure given in Method 5, Section 8.1, except the filter need not be weighed, and the 200 ml of 0.1N NaOH and Container 4 should be tared to within 0.5 g.

8.2 Preliminary Determinations. Follow the general procedure given in Method 5, Section 8.2, except select the nozzle size to maintain isokinetic sampling rates below 28 liters/min (1.0 cfm).

8.3 Preparation of Sampling Train. Follow the general procedure given in Method 5, Section 8.3.

8.4 Leak-Check Procedures. Same as Method 5, Section 8.4.

8.5 Sampling Train Operation. Follow the general procedure given in Method 5, Section 8.5, except maintain isokinetic sampling flow rates below 28 liters/min (1.0 cfm). For each run, record the data required on a data sheet similar to the one shown in Figure 108-2.

8.6 Calculation of Percent Isokinetic. Same as Method 5, Section 8.6.

8.7 Sample Recovery. Same as Method 5, Section 8.7, except that 0.1 N NaOH is used as the cleanup solvent instead of acetone and that the impinger water is treated as follows:

8.7.1 Container Number 4 (Impinger Water). Clean each of the first three impingers and connecting glassware in the following manner:

8.7.1.1 Wipe the impinger ball joints free of silicone grease, and cap the joints.

8.7.1.2 Rotate and agitate each of the first two impingers, using the impinger contents as a rinse solution.

8.7.1.3 Transfer the liquid from the first three impingers to Container Number 4. Remove the outlet ball-joint cap, and drain the contents through this opening. Do not separate the impinger parts (inner and outer tubes) while transferring their contents to the container.

8.7.1.4 Weigh the contents of Container No. 4 to within 0.5 g. Record in the log the weight of liquid along with a notation of any color or film observed in the impinger catch. The weight of liquid is needed along with the silica gel data to calculate the stack gas moisture content.

Note: Measure and record the total amount of 0.1 N NaOH used for rinsing under Sections 8.7.1.5 and 8.7.1.6.

8.7.1.5 Pour approximately 30 ml of 0.1 N NaOH into each of the first two impingers, and agitate the impingers. Drain the 0.1 N NaOH through the outlet arm of each impinger into Container Number 4. Repeat this operation a second time; inspect the impingers for any abnormal conditions.

8.7.1.6 Wipe the ball joints of the glassware connecting the impingers and the back half of the filter holder free of silicone grease, and rinse each piece of glassware twice with 0.1 N NaOH; transfer this rinse into Container Number 4. (DO NOT RINSE or brush the glass-fritted filter support.) Mark the height of the fluid level to determine whether leakage occurs during transport. Label the container to identify clearly its contents.

8.8 Blanks.	sample container labeled "NaOH blank."	Place these filters in a container labeled "filter blank."
8.8.1 Sodium Hydroxide. Save a portion of the 0.1 N NaOH used for cleanup as a blank. Take 200 ml of this solution directly from the wash bottle being used and place it in a plastic	8.8.2 Water. Save a sample of the water, and place it in a container labeled "H ₂ O blank."	9.0 Quality Control
	8.8.3 Filter. Save two filters from each lot of filters used in sampling.	9.1 Miscellaneous Quality Control Measures.

Section	Quality control measure	Effect
8.4, 10.1	Sampling equipment leak-checks and calibration	Ensures accuracy and precision of sampling measurements.
10.4	Spectrophotometer calibration	Ensures linearity of spectrophotometer response to standards.
11.5	Check for matrix effects	Eliminates matrix effects.
11.6	Audit sample analysis	Evaluates analyst's technique and standards preparation.

9.2 Volume Metering System Checks. Same as Method 5, Section 9.2.

10.0 Calibration and Standardization

Note: Maintain a laboratory log of all calibrations.

10.1 Sampling Equipment. Same as Method 5, Section 10.0.

10.2 Preparation of Standard Solutions.

10.2.1 For the high level procedure, pipet 1, 3, 5, 8, and 10 ml of the 1.0 mg As/ml stock solution into separate 100 ml volumetric flasks, each containing 5 ml of concentrated HNO₃. Dilute to the mark with water.

10.2.2 For the low level vapor generator procedure, pipet 1, 2, 3, and 5 ml of 1.0 µg As/ml standard solution into separate reaction tubes. Dilute to the mark with water.

10.2.3 For the low level graphite furnace procedure, pipet 1, 5, 10 and 15 ml of 1.0 µg As/ml standard solution into separate flasks along with 2 ml of the 5 percent nickel nitrate solution and 10 ml of the 3 percent H₂O₂ solution. Dilute to the mark with water.

10.3 Calibration Curve. Analyze a 0.8 N HNO₃ blank and each standard solution according to the procedures outlined in section 11.4.1. Repeat this procedure on each standard solution until two consecutive peaks agree within 3 percent of their average value. Subtract the average peak height (or peak area) of the blank—which must be less than 2 percent of recorder full scale—from the averaged peak height of each standard solution. If the blank absorbance is greater than 2 percent of full-scale, the probable cause is As contamination of a reagent or carry-over of As from a previous sample. Prepare the calibration curve by plotting the corrected peak height of each standard solution versus the corresponding final total As weight in the solution.

10.4 Spectrophotometer Calibration Quality Control. Calculate the least squares slope of the calibration curve. The line must pass through the origin or through a point no further from the

origin than ±2 percent of the recorder full scale. Multiply the corrected peak height by the reciprocal of the least squares slope to determine the distance each calibration point lies from the theoretical calibration line. The difference between the calculated concentration values and the actual concentrations (e.g., 1, 3, 5, 8, and 10 mg As for the high-level procedure) must be less than 7 percent for all standards.

Note: For instruments equipped with direct concentration readout devices, preparation of a standard curve will not be necessary. In all cases, follow calibration and operational procedures in the manufacturers' instruction manual.

11.0 Analytical Procedure

11.1 Sample Loss Check. Prior to analysis, check the liquid level in Containers Number 2 and Number 4. Note on the analytical data sheet whether leakage occurred during transport. If a noticeable amount of leakage occurred, either void the sample or take steps, subject to the approval of the Administrator, to adjust the final results.

11.2 Sample Preparation.

11.2.1 Container Number 1 (Filter). Place the filter and loose particulate matter in a 150 ml beaker. Also, add the filtered solid material from Container Number 2 (see Section 11.2.2). Add 50 ml of 0.1 N NaOH. Then stir and warm on a hot plate at low heat (do not boil) for about 15 minutes. Add 10 ml of concentrated HNO₃, bring to a boil, then simmer for about 15 minutes. Filter the solution through a glass fiber filter. Wash with hot water, and catch the filtrate in a clean 150 ml beaker. Boil the filtrate, and evaporate to dryness. Cool, add 5 ml of 50 percent HNO₃, and then warm and stir. Allow to cool. Transfer to a 50-ml volumetric flask, dilute to volume with water, and mix well.

11.2.2 Container Number 2 (Probe Wash).

11.2.2.1 Filter (using a glass fiber filter) the contents of Container Number

2 into a 200 ml volumetric flask. Combine the filtered (solid) material with the contents of Container Number 1 (Filter).

11.2.2.2 Dilute the filtrate to exactly 200 ml with water. Then pipet 50 ml into a 150 ml beaker. Add 10 ml of concentrated HNO₃, bring to a boil, and evaporate to dryness. Allow to cool, add 5 ml of 50 percent HNO₃, and then warm and stir. Allow the solution to cool, transfer to a 50-ml volumetric flask, dilute to volume with water, and mix well.

11.2.3 Container Number 4 (Impinger Solution). Transfer the contents of Container Number 4 to a 500 ml volumetric flask, and dilute to exactly 500-ml with water. Pipet 50 ml of the solution into a 150-ml beaker. Add 10 ml of concentrated HNO₃, bring to a boil, and evaporate to dryness. Allow to cool, add 5 ml of 50 percent HNO₃, and then warm and stir. Allow the solution to cool, transfer to a 50-ml volumetric flask, dilute to volume with water, and mix well.

11.2.4 Filter Blank. Cut each filter into strips, and treat each filter individually as directed in Section 11.2.1, beginning with the sentence, "Add 50 ml of 0.1 N NaOH."

11.2.5 Sodium Hydroxide and Water Blanks. Treat separately 50 ml of 0.1 N NaOH and 50 ml water, as directed under Section 11.2.3, beginning with the sentence, "Pipet 50 ml of the solution into a 150-ml beaker."

11.3 Spectrophotometer Preparation. Turn on the power; set the wavelength, slit width, and lamp current. Adjust the background corrector as instructed by the manufacturer's manual for the particular atomic absorption spectrophotometer. Adjust the burner and flame characteristics as necessary.

11.4 Analysis. Calibrate the analytical equipment and develop a calibration curve as outlined in Sections 10.2 through 10.4.

11.4.1 Arsenic Samples. Analyze an appropriately sized aliquot of each diluted sample (from Sections 11.2.1

through 11.2.3) until two consecutive peak heights agree within 3 percent of their average value. If applicable, follow the procedures outlined in Section 11.4.1.1. If the sample concentration falls outside the range of the calibration curve, make an appropriate dilution with 0.8 N HNO₃ so that the final concentration falls within the range of the curve. Using the calibration curve, determine the arsenic concentration in each sample fraction.

Note: Because instruments vary between manufacturers, no detailed operating instructions will be given here. Instead, the instrument manufacturer's detailed operating instructions should be followed.

11.4.1.1 Arsenic Determination at Low Concentration. The lower limit of flame AAS is 10 µg As/ml. If the arsenic concentration of any sample is at a lower level, use the graphite furnace or vapor generator which is available as an accessory component. Flame, graphite furnace, or vapor generators may be used for samples whose concentrations are between 10 and 30 µg/ml. Follow the manufacturer's instructions in the use of such equipment.

11.4.1.1.1 Vapor Generator Procedure. Place a sample containing between 0 and 5 µg of arsenic in the reaction tube, and dilute to 15 ml with water. Since there is some trial and error involved in this procedure, it may be necessary to screen the samples by conventional atomic absorption until an approximate concentration is determined. After determining the approximate concentration, adjust the volume of the sample accordingly. Pipet 15 ml of concentrated HCl into each tube. Add 1 ml of 30 percent KI solution. Place the reaction tube into a 50 °C (120 °F) water bath for 5 minutes. Cool to room temperature. Connect the reaction tube to the vapor generator assembly. When the instrument response has returned to baseline, inject 5.0 ml of 5 percent NaBH₄, and integrate the resulting spectrophotometer signal over a 30-second time period.

11.4.1.1.2 Graphite Furnace Procedure. Dilute the digested sample so that a 5 ml aliquot contains less than 1.5 µg of arsenic. Pipet 5 ml of this digested solution into a 10-ml volumetric flask. Add 1 ml of the 1 percent nickel nitrate solution, 0.5 ml of 50 percent HNO₃, and 1 ml of the 3 percent hydrogen peroxide and dilute to 10 ml with water. The sample is now ready for analysis.

11.4.1.2 Run a blank (0.8 N HNO₃) and standard at least after every five samples to check the spectrophotometer calibration. The peak height of the blank must pass through a point no further

from the origin than ±2 percent of the recorder full scale. The difference between the measured concentration of the standard (the product of the corrected average peak height and the reciprocal of the least squares slope) and the actual concentration of the standard must be less than 7 percent, or recalibration of the analyzer is required.

11.4.1.3 Determine the arsenic concentration in the filter blank (i.e., the average of the two blank values from each lot).

11.4.2 Container Number 3 (Silica Gel). This step may be conducted in the field. Weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g; record this weight.

11.5 Check for matrix effects on the arsenic results. Same as Method 12, Section 11.5.

11.6 Audit Sample Analysis.

11.6.1 When the method is used to analyze samples to demonstrate compliance with a source emission regulation, a set of EPA audit samples must be analyzed, subject to availability.

11.6.2 Concurrently analyze the audit samples and the compliance samples in the same manner to evaluate the technique of the analyst and the standards preparation.

Note: It is recommended that known quality control samples be analyzed prior to the compliance and audit sample analyses to optimize the system accuracy and precision. These quality control samples may be obtained by contacting the appropriate EPA regional Office or the responsible enforcement authority.

11.6.3 The same analyst, analytical reagents, and analytical system shall be used for the compliance samples and the EPA audit samples. If this condition is met, duplicate auditing of subsequent compliance analyses for the same enforcement agency within a 30-day period is waived. An audit sample set may not be used to validate different sets of compliance samples under the jurisdiction of separate enforcement agencies, unless prior arrangements have been made with both enforcement agencies.

11.7 Audit Sample Results.

11.7.1 Calculate the audit sample concentrations in g/m³ and submit results using the instructions provided with the audit samples.

11.7.2 Report the results of the audit samples and the compliance determination samples along with their identification numbers, and the analyst's name to the responsible enforcement authority. Include this information with reports of any subsequent compliance analyses for the same enforcement authority during the 30-day period.

11.7.3 The concentrations of the audit samples obtained by the analyst shall agree within 10 percent of the actual concentrations. If the 10 percent specification is not met, reanalyze the compliance and audit samples, and include initial and reanalysis values in the test report.

11.7.4 Failure to meet the 10 percent specification may require retests until the audit problems are resolved. However, if the audit results do not affect the compliance or noncompliance status of the affected facility, the Administrator may waive the reanalysis requirement, further audits, or retests and accept the results of the compliance test. While steps are being taken to resolve audit analysis problems, the Administrator may also choose to use the data to determine the compliance or noncompliance status of the affected facility.

12.0 Data Analysis and Calculations

12.1 Nomenclature.

B_{ws} = Water in the gas stream, proportion by volume.

C_a = Concentration of arsenic as read from the standard curve, µg/ml.

C_c = Actual audit concentration, g/m³.

C_d = Determined audit concentration, g/m³.

C_s = Arsenic concentration in stack gas, dry basis, converted to standard conditions, g/dsm³ (gr/dscf).

E_a = Arsenic mass emission rate, g/hr (lb/hr).

F_d = Dilution factor (equals 1 if the sample has not been diluted).

I = Percent of isokinetic sampling.

m_{bi} = Total mass of all four impingers and contents before sampling, g.

m_{fi} = Total mass of all four impingers and contents after sampling, g.

m_n = Total mass of arsenic collected in a specific part of the sampling train, µg.

m_t = Total mass of arsenic collected in the sampling train, µg.

T_m = Absolute average dry gas meter temperature (see Figure 108-2), °K (°R).

V_m = Volume of gas sample as measured by the dry gas meter, dry basis, m³ (ft³).

V_{m(std)} = Volume of gas sample as measured by the dry gas meter, corrected to standard conditions, m³ (ft³).

V_n = Volume of solution in which the arsenic is contained, ml.

V_{w(std)} = Volume of water vapor collected in the sampling train, corrected to standard conditions, m³ (ft³).

ΔH = Average pressure differential across the orifice meter (see Figure 108-2), mm H₂O (in. H₂O).

12.2 Average Dry Gas Meter Temperatures (T_m) and Average Orifice

Pressure Drop (ΔH). See data sheet (Figure 108-2).

to the procedures outlined in Method 5, Section 12.3.

12.3 Dry Gas Volume. Using data from this test, calculate $V_{m(std)}$ according

12.4 Volume of Water Vapor.

$$V_{w(std)} = K_2(m_{fi} - m_{bi}) \quad \text{Eq. 108-1}$$

Where:

$K_2 = 0.001334 \text{ m}^3/\text{g}$ for metric units.

$= 0.047012 \text{ ft}^3/\text{g}$ for English units.

12.5 Moisture Content.

$$B_{ws} = \frac{V_{w(std)}}{V_{m(std)} + V_{w(std)}} \quad \text{Eq. 108-2}$$

12.6 Amount of Arsenic Collected.

12.6.1 Calculate the amount of arsenic collected in each part of the sampling train, as follows:

$$m_n = C_a F_d V_n \quad \text{Eq. 108-3}$$

12.6.2 Calculate the total amount of arsenic collected in the sampling train as follows:

$$m_t = m_{(\text{filters})} + m_{(\text{probe})} + m_{(\text{impingers})} - m_{(\text{filter blank})} - m_{(\text{NaOH blank})} - m_{(\text{water blank})} \quad \text{Eq. 108-4}$$

12.7 Calculate the arsenic concentration in the stack gas (dry basis, adjusted to standard conditions) as follows:

$$C_s = K_3(m_t / V_{m(std)}) \quad \text{Eq. 108-5}$$

Where:

$K_3 = 10^{-6} \text{ g}/\mu\text{g}$ for metric units

$= 1.54 \times 10^{-5} \text{ gr}/\mu\text{g}$ for English units

12.8 Stack Gas Velocity and Volumetric Flow Rate. Calculate the average stack gas velocity and volumetric flow rate using data obtained in this method and the equations in Sections 12.2 and 12.3 of Method 2.

12.9 Pollutant Mass Rate. Calculate the arsenic mass emission rate as follows:

$$E_a = C_s Q_{sd} \quad \text{Eq. 108-6}$$

12.10 Isokinetic Variation. Same as Method 5, Section 12.11.

13.0 Method Performance

13.1 Sensitivity. The lower limit of flame AAS $10 \mu\text{g As/ml}$. The analytical procedure includes provisions for the use of a graphite furnace or vapor generator for samples with a lower arsenic concentration.

14.0 Pollution Prevention. [Reserved]

15.0 Waste Management. [Reserved]

16.0 References.

Same as References 1 through 9 of Method 5, Section 17.0, with the addition of the following:

1. Perkin Elmer Corporation. Analytical Methods for Atomic Absorption Spectrophotometry. 303-0152. Norwalk, Connecticut. September 1976. pp. 5-6.

2. Standard Specification for Reagent Water. In: Annual Book of American Society for Testing and Materials Standards. Part 31: Water, Atmospheric Analysis. American Society for Testing and Materials. Philadelphia, PA. 1974. pp. 40-42.

3. Stack Sampling Safety Manual (Draft). U.S. Environmental Protection Agency, Office of Air Quality Planning and Standard, Research Triangle Park, NC. September 1978.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

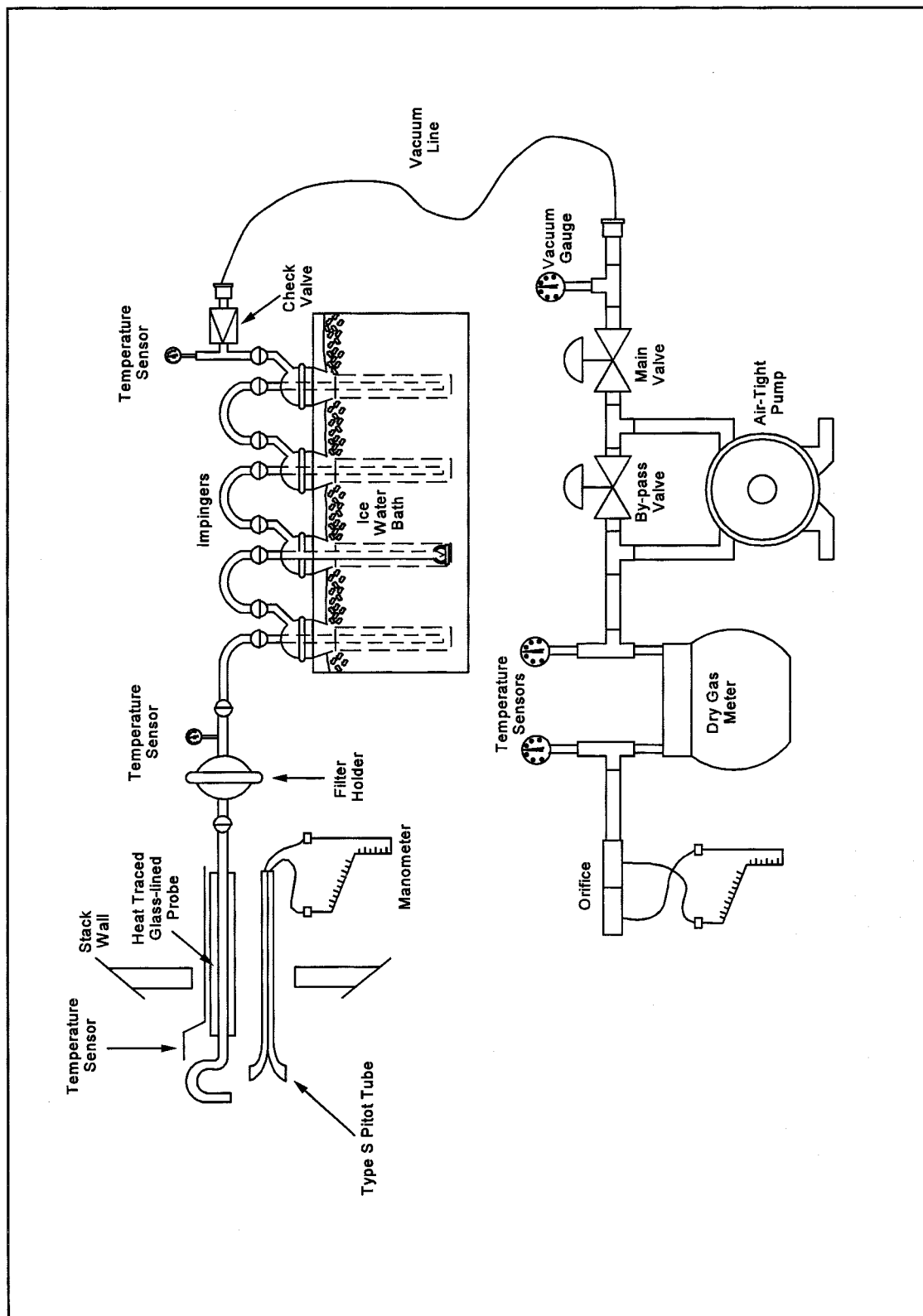


Figure 108-1. Arsenic Sampling Train

[illegible]

Method 108A—Determination of Arsenic Content in Ore Samples From Nonferrous Smelters

Note: This method does not include all of the specifications (e.g., equipment and

supplies) and procedures (e.g., sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in Appendix A to 40 CFR part 60. Therefore, to obtain reliable results,

persons using this method should have a thorough knowledge of Method 12.

1.0 Scope and Application**1.1 Analytes.**

Analyte	CAS No.	Sensitivity
Arsenic compounds as arsenic (As).	7440-38-2	Lower limit 10 µg/ml or less.

1.2 **Applicability.** This method applies to the determination of inorganic As content of process ore and reverberatory matte samples from nonferrous smelters and other sources as specified in an applicable subpart of the regulations.

1.3 **Data Quality Objectives.** Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

Arsenic bound in ore samples is liberated by acid digestion and analyzed by flame atomic absorption spectrophotometry (AAS).

3.0 Definitions [Reserved]**4.0 Interferences**

Analysis for As by flame AAS is sensitive to the chemical composition and to the physical properties (e.g., viscosity, pH) of the sample. The analytical procedure includes a check for matrix effects (section 11.5).

5.0 Safety

5.1 **Disclaimer.** This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

5.2 **Corrosive Reagents.** The following reagents are hazardous. Personal protective equipment and safe procedures that prevent chemical splashes are recommended. If contact occurs, immediately flush with copious amounts of water for at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burns as thermal burns.

5.2.1 **Hydrochloric Acid (HCl).** Highly corrosive liquid with toxic vapors. Vapors are highly irritating to eyes, skin, nose, and lungs, causing severe damage. May cause bronchitis, pneumonia, or edema of lungs. Exposure to concentrations of 0.13 to

0.2 percent can be lethal to humans in a few minutes. Provide ventilation to limit exposure. Reacts with metals, producing hydrogen gas.

5.2.2 **Hydrofluoric Acid (HF).** Highly corrosive to eyes, skin, nose, throat, and lungs. Reaction to exposure may be delayed by 24 hours or more. Provide ventilation to limit exposure.

5.2.3 **Hydrogen Peroxide (H₂O₂).** Very harmful to eyes. 30% H₂O₂ can burn skin, nose, and lungs.

5.2.4 **Nitric Acid (HNO₃).** Highly corrosive to eyes, skin, nose, and lungs. Vapors are highly toxic and can cause bronchitis, pneumonia, or edema of lungs. Reaction to inhalation may be delayed as long as 30 hours and still be fatal. Provide ventilation to limit exposure. Strong oxidizer. Hazardous reaction may occur with organic materials such as solvents.

5.2.5 **Sodium Hydroxide (NaOH).** Causes severe damage to eyes and skin. Inhalation causes irritation to nose, throat, and lungs. Reacts exothermically with limited amounts of water.

6.0 Equipment and Supplies

6.1 **Sample Collection and Preparation.** The following items are required for sample collection and preparation:

6.1.1 **Parr Acid Digestion Bomb.** Stainless steel with vapor-tight Teflon cup and cover.

6.1.2 **Volumetric Pipets.** 2- and 5-ml sizes.

6.1.3 **Volumetric Flask.** 50-ml polypropylene with screw caps, (one needed per standard).

6.1.4 **Funnel.** Polyethylene or polypropylene.

6.1.5 **Oven.** Capable of maintaining a temperature of approximately 105 °C (221 °F).

6.1.6 **Analytical Balance.** To measure to within 0.1 mg.

6.2 **Analysis.** The following items are required for analysis:

6.2.1 **Spectrophotometer and Recorder.** Equipped with an electrodeless discharge lamp and a background corrector to measure absorbance at 193.7 nm. For measuring samples having less than 10 µg As/ml,

use a graphite furnace or vapor generator accessory. The recorder shall match the output of the spectrophotometer.

6.2.2 **Volumetric Flasks.** Class A, 50-ml (one needed per sample and blank), 500-ml, and 1-liter.

6.2.3 **Volumetric Pipets.** Class A, 1-, 5-, 10-, and 25-ml sizes.

7.0 Reagents and Standards.

Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available; otherwise, use the best available grade.

7.1 **Sample Collection and Preparation.** The following reagents are required for sample collection and preparation:

7.1.1 **Water.** Deionized distilled to meet ASTM D 1193-77 or 91 Type 3 (incorporated by reference—See § 61.18). When high concentrations of organic matter are not expected to be present, the KMnO₄ test for oxidizable organic matter may be omitted. Use in all dilutions requiring water.

7.1.2 **Nitric Acid Concentrated.**

7.1.3 **Nitric Acid, 0.5 N.** In a 1-liter volumetric flask containing water, add 32 ml of concentrated HNO₃ and dilute to volume with water.

7.1.4 **Hydrofluoric Acid, Concentrated.**

7.1.5 **Potassium Chloride (KCl) Solution,** 10 percent weight by volume (W/V). Dissolve 10 g KCl in water, add 3 ml concentrated HNO₃, and dilute to 100 ml.

7.1.6 **Filter.** Teflon filters, 3-micron porosity, 47-mm size. (Available from Millipore Co., type FS, Catalog Number FSLW04700.)

7.1.7 **Sodium Borohydride (NaBH₄), 5 Percent (W/V).** Dissolve 50.0 g of NaBH₄ in about 500 ml of 0.1 N NaOH in a 1-liter volumetric flask. Then, dilute to exactly 1.0 liter with 0.1 N NaOH.

7.1.8 **Nickel Nitrate, 5 Percent Ni (W/V).** Dissolve 24.780 g of nickel nitrate hexahydrate [Ni(NO₃)₂ · 6H₂O] in water in a 100-ml volumetric flask, and dilute to 100 ml with water.

7.1.9 Nickel Nitrate, 1 Percent Ni (W/V). Pipet 20 ml of 5 percent nickel nitrate solution into a 100-ml volumetric flask, and dilute to 100 ml with water.

7.2 Analysis. The following reagents and standards are required for analysis:

7.2.1 Water. Same as in Section 7.1.1.

7.2.2 Sodium Hydroxide, 0.1 N. Dissolve 2.00 g of NaOH in water in a 500-ml volumetric flask. Dilute to volume with water.

7.2.3 Nitric Acid, 0.5 N. Same as in Section 7.1.3.

7.2.4 Potassium Chloride Solution, 10 percent. Same as in Section 7.1.5.

7.2.5 Hydrochloric Acid, Concentrated.

7.2.6 Potassium Iodide (KI), 30 Percent (W/V). Dissolve 300 g of KI in about 500 ml of water in a 1-liter

volumetric flask. Then, dilute to exactly 1.0 liter with water.

7.2.7 Hydrogen Peroxide, 3 Percent by Volume. Pipet 50 ml of 30 percent H_2O_2 into a 500-ml volumetric flask, and dilute to exactly 500 ml with water.

7.2.8 Stock Arsenic Standard, 1 mg As/ml. Dissolve 1.3203 g of primary grade As_2O_3 in 20 ml of 0.1 N NaOH. Slowly add 30 ml of concentrated HNO_3 , and heat in an oven at 105 °C (221 °F) for 2 hours. Allow to cool, and dilute to 1 liter with deionized distilled water.

7.2.9 Nitrous Oxide. Suitable quality for AAS analysis.

7.2.10 Acetylene. Suitable quality for AAS analysis.

7.2.11 Quality Assurance Audit Samples. When making compliance determinations, and upon availability, audit samples may be obtained from the

appropriate EPA regional Office or from the responsible enforcement authority.

Note: The responsible enforcement authority should be notified at least 30 days prior to the test date to allow sufficient time for sample delivery.

8.0 Sample Collection, Preservation, Transport, and Storage

8.1 Sample Collection. A sample that is representative of the ore lot to be tested must be taken prior to analysis. (A portion of the samples routinely collected for metals analysis may be used provided the sample is representative of the ore being tested.)

8.2 Sample Preparation. The sample must be ground into a finely pulverized state.

9.0 Quality Control

Section	Quality control measure	Effect
10.2	Spectrophotometer calibration	Ensure linearity of spectrophotometer response to standards.
11.5	Check for matrix effects	Eliminate matrix effects
11.6	Audit sample analysis	Evaluate analyst's technique and standards preparation.

10.0 Calibration and Standardizations

Note: Maintain a laboratory log of all calibrations.

10.1 Preparation of Standard Solutions. Pipet 1, 5, 10, and 25 ml of the stock As solution into separate 100-ml volumetric flasks. Add 10 ml KCl solution and dilute to the mark with 0.5 N HNO_3 . This will give standard concentrations of 10, 50, 100, and 250 μg As/ml. For low-level arsenic samples that require the use of a graphite furnace or vapor generator, follow the procedures in Section 11.3.1. Dilute 10 ml of KCl solution to 100 ml with 0.5 N HNO_3 and use as a reagent blank.

10.2 Calibration Curve. Analyze the reagent blank and each standard solution according to the procedures outlined in Section 11.3. Repeat this procedure on each standard solution until two consecutive peaks agree within 3 percent of their average value. Subtract the average peak height (or peak area) of the blank—which must be less than 2 percent of recorder full scale—from the averaged peak heights of each standard solution. If the blank absorbance is greater than 2 percent of full-scale, the probable cause is Hg contamination of a reagent or carry-over of As from a previous sample. Prepare the calibration curve by plotting the corrected peak height of each standard solution versus the corresponding final total As weight in the solution.

10.3 Spectrophotometer Calibration Quality Control. Calculate the least

squares slope of the calibration curve. The line must pass through the origin or through a point no further from the origin than ± 2 percent of the recorder full scale. Multiply the corrected peak height by the reciprocal of the least squares slope to determine the distance each calibration point lies from the theoretical calibration line. The difference between the calculated concentration values and the actual concentrations must be less than 7 percent for all standards.

Note: For instruments equipped with direct concentration readout devices, preparation of a standard curve will not be necessary. In all cases, follow calibration and operational procedures in the manufacturer's instruction manual.

11.0 Analytical Procedure

11.1 Sample Preparation. Weigh 50 to 500 mg of finely pulverized sample to the nearest 0.1 mg. Transfer the sample into the Teflon cup of the digestion bomb, and add 2 ml each of concentrated HNO_3 and HF. Seal the bomb immediately to prevent the loss of any volatile arsenic compounds that may form. Heat in an oven at 105 °C (221 °F) for 2 hours. Remove the bomb from the oven and allow to cool. Using a Teflon filter, quantitatively filter the digested sample into a 50-ml polypropylene volumetric flask. Rinse the bomb three times with small portions of 0.5 N HNO_3 , and filter the rinses into the flask. Add 5 ml of KCl

solution to the flask, and dilute to 50 ml with 0.5 N HNO_3 .

11.2 Spectrophotometer Preparation.

11.2.1 Turn on the power; set the wavelength, slit width, and lamp current. Adjust the background corrector as instructed by the manufacturer's manual for the particular atomic absorption spectrophotometer. Adjust the burner and flame characteristics as necessary.

11.2.2 Develop a spectrophotometer calibration curve as outlined in Sections 10.2 and 10.3.

11.3 Arsenic Determination.

Analyze an appropriately sized aliquot of each diluted sample (from Section 11.1) until two consecutive peak heights agree within 3 percent of their average value. If applicable, follow the procedures outlined in Section 11.3.1. If the sample concentration falls outside the range of the calibration curve, make an appropriate dilution with 0.5 N HNO_3 so that the final concentration falls within the range of the curve. Using the calibration curve, determine the As concentration in each sample.

Note: Because instruments vary between manufacturers, no detailed operating instructions will be given here. Instead, the instrument manufacturer's detailed operating instructions should be followed.

11.3.1 Arsenic Determination at Low Concentration. The lower limit of flame AAS is 10 μg As/ml. If the arsenic concentration of any sample is at a lower level, use the vapor generator or graphite furnace which is available as

an accessory component. Flame, graphite furnace, or vapor generators may be used for samples whose concentrations are between 10 and 30 µg/ml. Follow the manufacturer's instructions in the use of such equipment.

11.3.1.1 Vapor Generator Procedure. Place a sample containing between 0 and 5 µg of arsenic in the reaction tube, and dilute to 15 ml with water. Since there is some trial and error involved in this procedure, it may be necessary to screen the samples by conventional AAS until an approximate concentration is determined. After determining the approximate concentration, adjust the volume of the sample accordingly. Pipet 15 ml of concentrated HCl into each tube. Add 1 ml of 30 percent KI solution. Place the reaction tube into a 50 °C (120 °F) water bath for 5 minutes. Cool to room temperature. Connect the reaction tube to the vapor generator assembly. When the instrument response has returned to baseline, inject 5.0 ml of 5 percent NaBH₄ and integrate the resulting spectrophotometer signal over a 30-second time period.

11.3.1.2 Graphite Furnace Procedure. Pipet 5 ml of the digested solution into a 10-ml volumetric flask. Add 1 ml of the 1 percent nickel nitrate solution, 0.5 ml of 50 percent HNO₃, and 1 ml of the 3 percent H₂O₂, and dilute to 10 ml with water. The sample is now ready to inject in the furnace for analysis.

11.4 Run a blank and standard at least after every five samples to check the spectrophotometer calibration. The peak height of the blank must pass through a point no further from the

origin than ±2 percent of the recorder full scale. The difference between the measured concentration of the standard (the product of the corrected average peak height and the reciprocal of the least squares slope) and the actual concentration of the standard must be less than 7 percent, or recalibration of the analyzer is required.

11.5 Mandatory Check for Matrix Effects on the Arsenic Results. Same as Method 12, Section 11.5.

11.6 Audit Sample Analysis.

11.6.1 When the method is used to analyze samples to demonstrate compliance with a source emission regulation, a set of EPA audit samples must be analyzed, subject to availability.

11.6.2 Concurrently analyze the audit samples and the compliance samples in the same manner to evaluate the technique of the analyst and the standards preparation.

Note: It is recommended that known quality control samples be analyzed prior to the compliance and audit sample analyses to optimize the system accuracy and precision. These quality control samples may be obtained by contacting the appropriate EPA regional Office or the responsible enforcement authority.

11.6.3 The same analyst, analytical reagents, and analytical system shall be used for the compliance samples and the EPA audit samples. If this condition is met, duplicate auditing of subsequent compliance analyses for the same enforcement agency within a 30-day period is waived. An audit sample set may not be used to validate different sets of compliance samples under the jurisdiction of separate enforcement agencies, unless prior arrangements

have been made with both enforcement agencies.

11.7 Audit Sample Results.

11.7.1 Calculate the audit sample concentrations in g/m³ and submit results using the instructions provided with the audit samples.

11.7.2 Report the results of the audit samples and the compliance determination samples along with their identification numbers, and the analyst's name to the responsible enforcement authority. Include this information with reports of any subsequent compliance analyses for the same enforcement authority during the 30-day period.

11.7.3 The concentrations of the audit samples obtained by the analyst shall agree within 10 percent of the actual concentrations. If the 10 percent specification is not met, reanalyze the compliance and audit samples, and include initial and reanalysis values in the test report.

11.7.4 Failure to meet the 10 percent specification may require retests until the audit problems are resolved. However, if the audit results do not affect the compliance or noncompliance status of the affected facility, the Administrator may waive the reanalysis requirement, further audits, or retests and accept the results of the compliance test. While steps are being taken to resolve audit analysis problems, the Administrator may also choose to use the data to determine the compliance or noncompliance status of the affected facility.

12.0 Data Analysis and Calculations

12.1 Calculate the percent arsenic in the ore sample as follows:

$$\% \text{ As} = \frac{5C_a F_d}{W} \quad \text{Eq. 108A-1}$$

Where:

C_a = Concentration of As as read from the standard curve, µg/ml.

F_d = Dilution factor (equals to 1 if the sample has not been diluted).

W = Weight of ore sample analyzed, mg.
5 = (50 ml sample " 100)/(10³ µg/mg).

13.0 Method Performance

13.1 Sensitivity. The lower limit of flame AAS is 10 µg As/ml. The analytical procedure includes provisions for the use of a graphite furnace or vapor generator for samples with a lower arsenic concentration.

14.0 Pollution Prevention. [Reserved]

15.0 Waste Management. [Reserved]

16.0 References

Same as References 1 through 9 of Section 17.0 of Method 5, with the addition of the following:

1. Perkin Elmer Corporation. Analytical Methods of Atomic Absorption Spectrophotometry. 303-0152. Norwalk, Connecticut. September 1976. pp 5-6.

2. Ringwald, D. Arsenic Determination on Process Materials from ASARCO's Copper Smelter in Tacoma, Washington. Unpublished Report. Prepared for Emission Measurement Branch, Emission Standards and Engineering Division, U.S. Environmental Protection Agency, Research

Triangle Park, North Carolina. August 1980. 35 pp.

3. Stack Sampling Safety Manual (Draft). U.S. Environmental Protection Agency, Office of Air Quality Planning and Standard, Research Triangle Park, NC. September 1978.

17.0 Tables, Diagrams, Flowcharts, and Validation Data. [Reserved]

Method 108B—Determination of Arsenic Content in Ore Samples From Nonferrous Smelters

Note: This method does not include all of the specifications (e.g., equipment and supplies) and procedures (e.g., sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this appendix and in Appendix A to 40 CFR Part 60. Therefore, to

obtain reliable results, persons using this method should have a thorough knowledge

of at least the following additional test methods: Method 12 and Method 108A.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Arsenic compounds as arsenic (As).	7440-38-2	Lower limit 10 µg/ml.

1.2 Applicability. This method applies to the determination of inorganic As content of process ore and reverberatory matte samples from nonferrous smelters and other sources as specified in an applicable subpart of the regulations. Samples resulting in an analytical concentration greater than 10 µg As/ml may be analyzed by this method. For lower level arsenic samples, Method 108C should be used.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

Arsenic bound in ore samples is liberated by acid digestion and analyzed by flame atomic absorption spectrophotometry (AAS).

3.0 Definitions [Reserved]

4.0 Interferences

Analysis for As by flame AAS is sensitive to the chemical composition and to the physical properties (*e.g.*, viscosity, pH) of the sample. The analytical procedure includes a check for matrix effects (Section 11.4).

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive Reagents. The following reagents are hazardous. Personal protective equipment and safe procedures that prevent chemical splashes are recommended. If contact occurs, immediately flush with copious amounts of water for at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burns as thermal burns.

5.2.1 Hydrochloric acid (HCl). Highly corrosive liquid with toxic

vapors. Vapors are highly irritating to eyes, skin, nose, and lungs, causing severe damage. May cause bronchitis, pneumonia, or edema of lungs. Exposure to concentrations of 0.13 to 0.2 percent can be lethal to humans in a few minutes. Provide ventilation to limit exposure. Reacts with metals, producing hydrogen gas.

5.2.2 Hydrofluoric Acid (HF). Highly corrosive to eyes, skin, nose, throat, and lungs. Reaction to exposure may be delayed by 24 hours or more. Provide ventilation to limit exposure.

5.2.3 Nitric Acid (HNO₃). Highly corrosive to eyes, skin, nose, and lungs. Vapors are highly toxic and can cause bronchitis, pneumonia, or edema of lungs. Reaction to inhalation may be delayed as long as 30 hours and still be fatal. Provide ventilation to limit exposure. Strong oxidizer. Hazardous reaction may occur with organic materials such as solvents.

5.2.4 Perchloric Acid (HClO₄). Corrosive to eyes, skin, nose, and throat. Provide ventilation to limit exposure. Very strong oxidizer. Keep separate from water and oxidizable materials to prevent vigorous evolution of heat, spontaneous combustion, or explosion. Heat solutions containing HClO₄ only in hoods specifically designed for HClO₄.

6.0 Equipment and Supplies

6.1 Sample Preparation. The following items are required for sample preparation:

6.1.1 Teflon Beakers. 150-ml.

6.1.2 Graduated Pipets. 5-ml disposable.

6.1.3 Graduated Cylinder. 50-ml.

6.1.4 Volumetric Flask. 100-ml.

6.1.5 Analytical Balance. To measure within 0.1 mg.

6.1.6 Hot Plate.

6.1.7 Perchloric Acid Fume Hood.

6.2 Analysis. The following items are required for analysis:

6.2.1 Spectrophotometer. Equipped with an electrodeless discharge lamp and a background corrector to measure absorbance at 193.7 nm.

6.2.2 Beaker and Watch Glass. 400-ml.

6.2.3 Volumetric Flask. 1-liter.

6.2.4 Volumetric Pipets. 1-, 5-, 10-, and 25-ml.

7.0 Reagents and Standards

Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available; otherwise, use the best available grade.

7.1 Sample Preparation. The following reagents are required for sample preparation:

7.1.1 Water. Deionized distilled to meet ASTM D 1193-77 or 91 Type 3 (incorporated by reference—see § 61.18).

7.1.2 Nitric Acid, Concentrated.

7.1.3 Hydrofluoric Acid, Concentrated.

7.1.4 Perchloric Acid, 70 Percent.

7.1.5 Hydrochloric Acid, Concentrated.

7.2 Analysis. The following reagents and standards are required for analysis:

7.2.1 Water. Same as in Section 7.1.1.

7.2.2 Stock Arsenic Standard, 1.0 mg As/ml. Dissolve 1.3203 g of primary grade As₂O₃ [dried at 105 °C (221 °F)] in a 400-ml beaker with 10 ml of HNO₃ and 5 ml of HCl. Cover with a watch glass, and heat gently until dissolution is complete. Add 10 ml of HNO₃ and 25 ml of HClO₄, evaporate to strong fumes of HClO₄, and reduce to about 20 ml volume. Cool, add 100 ml of water and 100 ml of HCl, and transfer quantitatively to a 1-liter volumetric flask. Dilute to volume with water and mix.

7.2.3 Acetylene. Suitable quality for AAS analysis.

7.2.4 Air. Suitable quality for AAS analysis.

7.2.5 Quality Assurance Audit Samples. Same as in Method 108A, Section 7.2.11.

8.0 Sample Collection, Preservation, Transport, and Storage

Same as in Method 108A, Sections 8.1 and 8.2.

9.0 Quality Control

Section	Quality control measure	Effect
10.2	Spectrophotometer calibration	Ensure linearity of spectrophotometer response to standards.

Section	Quality control measure	Effect
11.4	Check for matrix effects	Eliminate matrix effects.
11.5	Audit sample analysis	Evaluate analyst's technique and standards preparation.

10.0 Calibration and Standardization

Note: Maintain a laboratory log of all calibrations.

10.1 Preparation of Standard Solutions. Pipet 1, 5, 10, and 25 ml of the stock As solution into separate 100-ml volumetric flasks. Add 2 ml of HClO₄, 10 ml of HCl, and dilute to the mark with water. This will provide standard concentrations of 10, 50, 100, and 250 µg As/ml.

10.2 Calibration Curve and Spectrophotometer Calibration Quality Control. Same as Method 108A, Sections 10.2 and 10.3

11.0 Analytical Procedure

11.1 Sample Preparation. Weigh 100 to 1000 mg of finely pulverized sample to the nearest 0.1 mg. Transfer the sample to a 150-ml Teflon beaker. Dissolve the sample by adding 15 ml of HNO₃, 10 ml of HCl, 10 ml of HF, and 10 ml of HClO₄ in the exact order as described, and let stand for 10 minutes. In a HClO₄ fume hood, heat on a hot plate until 2–3 ml of HClO₄ remain, then cool. Add 20 ml of water and 10 ml of HCl. Cover and warm until the soluble salts are in solution. Cool, and transfer quantitatively to a 100-ml volumetric flask. Dilute to the mark with water.

11.2 Spectrophotometer Preparation. Same as in Method 108A, Section 11.2.

11.3 Arsenic Determination. If the sample concentration falls outside the range of the calibration curve, make an appropriate dilution with 2 percent HClO₄/10 percent HCl (prepared by diluting 2 ml concentrated HClO₄ and 10 ml concentrated HCl to 100 ml with water) so that the final concentration falls within the range of the curve. Using the calibration curve, determine the As concentration in each sample.

Note: Because instruments vary between manufacturers, no detailed operating instructions will be given here. Instead, the instrument manufacturer's detailed operating instructions should be followed.

Run a blank and standard at least after every five samples to check the spectrophotometer calibration. The peak height of the blank must pass through a point no further from the origin than ±2 percent of the recorder full scale. The difference between the measured concentration of the standard (the product of the corrected average peak height and the reciprocal of the least squares slope) and the actual concentration of the standard must be less than 7 percent, or recalibration of the analyzer is required.

11.4 Mandatory Check for Matrix Effects on the Arsenic Results. Same as Method 12, Section 11.5.

11.5 Audit Sample Analysis. Same as in Method 108A, Section 11.6.

12.0 Data Analysis and Calculations

Same as in Method 108A, Section 12.0.

13.0 Method Performance

13.1 Sensitivity. The lower limit of flame AAS is 10 µg As/ml.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

Same as in Method 108A, Section 16.0.

17.0 Tables, Diagrams, Flowcharts, and Validation Data [Reserved]

Method 108C—Determination of Arsenic Content in Ore Samples From Nonferrous Smelters (Molybdenum Blue Photometric Procedure)

Note: This method does not include all of the specifications (e.g., equipment and supplies) and procedures (e.g., sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least Method 108A.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Arsenic compounds as arsenic (As).	7440–38–2	Lower limit 0.0002 percent As by weight.

1.2 Applicability. This method applies to the determination of inorganic As content of process ore and reverberatory matte samples from nonferrous smelters and other sources as specified in an applicable subpart of the regulations.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

Arsenic bound in ore samples is liberated by acid digestion and analyzed by the molybdenum blue photometric procedure.

3.0 Definitions. [Reserved]

4.0 Interferences. [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive Reagents. The following reagents are hazardous. Personal protective equipment and safe procedures that prevent chemical splashes are recommended. If contact occurs, immediately flush with copious

amounts of water for at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burns as thermal burns.

5.2.1 Hydrochloric Acid (HCl). Highly corrosive liquid with toxic vapors. Vapors are highly irritating to eyes, skin, nose, and lungs, causing severe damage. May cause bronchitis, pneumonia, or edema of lungs. Exposure to concentrations of 0.13 to 0.2 percent can be lethal to humans in a few minutes. Provide ventilation to limit exposure. Reacts with metals, producing hydrogen gas.

5.2.2 Hydrofluoric Acid (HF). Highly corrosive to eyes, skin, nose, throat, and lungs. Reaction to exposure may be delayed by 24 hours or more. Provide ventilation to limit exposure.

5.2.3 Nitric Acid (HNO₃). Highly corrosive to eyes, skin, nose, and lungs. Vapors are highly toxic and can cause bronchitis, pneumonia, or edema of lungs. Reaction to inhalation may be delayed as long as 30 hours and still be fatal. Provide ventilation to limit exposure. Strong oxidizer. Hazardous reaction may occur with organic materials such as solvents.

5.2.4 Perchloric Acid (HClO₄). Corrosive to eyes, skin, nose, and throat. Provide ventilation to limit exposure. Very strong oxidizer. Keep separate from water and oxidizable materials to prevent vigorous evolution of heat, spontaneous combustion, or explosion. Heat solutions containing HClO₄ only in hoods specifically designed for HClO₄.

5.2.5 Sulfuric acid (H₂SO₄). Rapidly destructive to body tissue. Will cause third degree burns. Eye damage may result in blindness. Inhalation may be fatal from spasm of the larynx, usually within 30 minutes. May cause lung tissue damage with edema. 3 mg/m³ will cause lung damage in uninitiated. 1 mg/m³ for 8 hours will cause lung damage or, in higher concentrations, death. Provide ventilation to limit inhalation. Reacts violently with metals and organics.

6.0 Equipment and Supplies

6.1 Sample Preparation. The following items are required for sample preparation:

- 6.1.1 Analytical Balance. To measure to within 0.1 mg.
- 6.1.2 Erlenmeyer Flask. 300-ml.
- 6.1.3 Hot Plate.
- 6.1.4 Distillation Apparatus. No. 6, in ASTM E 50–82, 86, or 90 (Reapproved 1995)(incorporated by

reference—see § 61.18); detailed in Figure 108C–1.

6.1.5 Graduated Cylinder. 50-ml.

6.1.6 Perchloric Acid Fume Hood.

6.2 Analysis. The following items are required for analysis:

6.2.1 Spectrophotometer. Capable of measuring at 660 nm.

6.2.2 Volumetric Flasks. 50- and 100-ml.

7.0 Reagents and Standards

Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available; otherwise, use the best available grade.

7.1 Sample Preparation. The following reagents are required for sample preparation:

7.1.1 Water. Deionized distilled to meet ASTM D 1193–77 or 91 Type 3 (incorporated by reference—see § 61.18). When high concentrations of organic matter are not expected to be present, the KMnO₄ test for oxidizable organic matter may be omitted. Use in all dilutions requiring water.

7.1.2 Nitric Acid, Concentrated.

7.1.3 Hydrofluoric Acid, Concentrated.

7.1.4 Sulfuric Acid, Concentrated.

7.1.5 Perchloric Acid, 70 Percent.

7.1.6 Hydrochloric Acid, Concentrated.

7.1.7 Dilute Hydrochloric Acid. Add one part concentrated HCl to nine parts water.

7.1.8 Hydrazine Sulfate ((NH₂)₂·H₂SO₄).

7.1.9 Potassium Bromide (KBr).

7.1.10 Bromine Water, Saturated.

7.2 Analysis. The following reagents and standards are required for analysis:

7.2.1 Water. Same as in Section

7.1.1.

7.2.2 Methyl Orange Solution, 1 g/liter.

7.2.3 Ammonium Molybdate Solution, 5 g/liter. Dissolve 0.5 g (NH₄)Mo₇O₂₄·4H₂O in water in a 100-ml volumetric flask, and dilute to the mark. This solution must be freshly prepared.

7.2.4 Standard Arsenic Solution, 10 µg As/ml. Dissolve 0.13203 g of As₂O₃ in 100 ml HCl in a 1-liter volumetric flask. Add 200 ml of water, cool, dilute to the mark with water, and mix. Transfer 100 ml of this solution to a 1-liter volumetric flask, add 40 ml HCl, cool, dilute to the mark, and mix.

7.2.5 Hydrazine Sulfate Solution, 1 g/liter. Dissolve 0.1 g of [(NH₂)₂·H₂SO₄] in water, and dilute to 100 ml in a volumetric flask. This solution must be freshly prepared.

7.2.6 Potassium Bromate (KBrO₃) Solution, 0.03 Percent Weight by Volume (W/V). Dissolve 0.3 g KBrO₃ in water, and dilute to 1 liter with water.

7.2.7 Ammonium Hydroxide (NH₄OH), Concentrated.

7.2.8 Boiling Granules.

7.2.9 Hydrochloric Acid, 50 percent by volume. Dilute equal parts concentrated HCl with water.

7.2.10 Quality Assurance Audit Samples. Same as in Method 108A, Section 7.2.11.

8.0 Sample Collection, Preservation, Transport, and Storage

Same as in Method 108A, Sections 8.1 and 8.2.

9.0 Quality Control

Section	Quality control measure	Effect
10.2	Calibration curve preparation	Ensure linearity of spectrophotometric analysis of standards. Evaluate analyst's technique and standards preparation.
11.3	Audit sample analysis	

10.0 Calibration and Standardizations

Note: Maintain a laboratory log of all calibrations.

10.1 Preparation of Standard Solutions. Transfer 1.0, 2.0, 4.0, 8.0, 12.0, 16.0, and 20.0 ml of standard arsenic solution (10 µg/ml) to each of seven 50-ml volumetric flasks. Dilute to 20 ml with dilute HCl. Add one drop of methyl orange solution and neutralize to the yellow color with dropwise addition of NH₄OH. Just bring back to the red color by dropwise addition of dilute HCl, and add 10 ml in excess. Proceed with the color development as described in Section 11.2.

10.2 Calibration Curve. Plot the spectrophotometric readings of the calibration solutions against µg As per 50 ml of solution. Use this curve to determine the As concentration of each sample.

10.3 Spectrophotometer Calibration Quality Control. Calculate the least squares slope of the calibration curve. The line must pass through the origin or through a point no further from the origin than ±2 percent of the recorder full scale. Multiply the corrected peak height by the reciprocal of the least squares slope to determine the distance each calibration point lies from the theoretical calibration line. The

difference between the calculated concentration values and the actual concentrations must be less than 7 percent for all standards.

11.0 Analytical Procedure

11.1 Sample Preparation.

11.1.1 Weigh 1.0 g of finely pulverized sample to the nearest 0.1 mg. Transfer the sample to a 300 ml Erlenmeyer flask and add 15 ml of HNO₃, 4 ml HCl, 2 ml HF, 3 ml HClO₄, and 15 ml H₂SO₄, in the order listed. In a HClO₄ fume hood, heat on a hot plate to decompose the sample. Then heat while swirling over an open flame until dense white fumes evolve. Cool, add 15

ml of water, swirl to hydrate the H_2SO_4 completely, and add several boiling granules. Cool to room temperature.

11.1.2 Add 1 g of KBr, 1 g hydrazine sulfate, and 50 ml HCl. Immediately attach the distillation head with thermometer and dip the side arm into a 50-ml graduated cylinder containing 25 ml of water and 2 ml of bromine water. Keep the graduated cylinder immersed in a beaker of cold water during distillation. Distill until the temperature of the vapor in the flask reaches 107 °C (225 °F). When distillation is complete, remove the flask from the hot plate, and simultaneously wash down the side arm with water as it is removed from the cylinder.

11.1.3 If the expected arsenic content is in the range of 0.0020 to 0.10 percent, dilute the distillate to the 50-ml mark of the cylinder with water, stopper, and mix. Transfer a 5.0-ml aliquot to a 50-ml volumetric flask. Add 10 ml of water and a boiling granule. Place the flask on a hot plate, and heat gently until the bromine is expelled and the color of methyl orange indicator persists upon the addition of 1 to 2 drops. Cool the flask to room temperature. Neutralize just to the yellow color of the indicator with dropwise additions of NH_4OH . Bring back to the red color by dropwise addition of dilute HCl, and add 10 ml excess. Proceed with the molybdenum blue color development as described in Section 11.2.

11.1.4 If the expected arsenic content is in the range of 0.0002 to 0.0010 percent As, transfer either the entire initial distillate or the measured remaining distillate from Section 11.1.2 to a 250-ml beaker. Wash the cylinder

with two successive portions of concentrated HNO_3 , adding each portion to the distillate in the beaker. Add 4 ml of concentrated HClO_4 , a boiling granule, and cover with a flat watch glass placed slightly to one side. Boil gently on a hot plate until the volume is reduced to approximately 10 ml. Add 3 ml of HNO_3 , and continue the evaporation until HClO_4 is refluxing on the beaker cover. Cool briefly, rinse the underside of the watch glass and the inside of the beaker with about 3–5 ml of water, cover, and continue the evaporation to expel all but 2 ml of the HClO_4 .

Note: If the solution appears cloudy due to a small amount of antimony distilling over, add 4 ml of 50 percent HCl and 5 ml of water, cover, and warm gently until clear. If cloudiness persists, add 5 ml of HNO_3 and 2 ml H_2SO_4 . Continue the evaporation of volatile acids to solubilize the antimony until dense white fumes of H_2SO_4 appear. Retain at least 1 ml of the H_2SO_4 .

11.1.5 To the 2 ml of HClO_4 solution or 1 ml of H_2SO_4 solution, add 15 ml of water, boil gently for 2 minutes, and then cool. Proceed with the molybdenum blue color development by neutralizing the solution directly in the beaker just to the yellow indicator color by dropwise addition of NH_4OH . Obtain the red color by dropwise addition of dilute HCl. Transfer the solution to a 50-ml volumetric flask. Rinse the beaker successively with 10 ml of dilute HCl, followed by several small portions of water. At this point the volume of solution in the flask should be no more than 40 ml. Continue with the color development as described in Section 11.2.

11.2 Analysis.

11.2.1 Add 1 ml of KBrO_3 solution to the flask and heat on a low-

temperature hot plate to about 50 °C (122 °F) to oxidize the arsenic and methyl orange. Add 5.0 ml of ammonium molybdate solution to the warm solution and mix. Add 2.0 ml of hydrazine sulfate solution, dilute until the solution comes within the neck of the flask, and mix. Place the flask in a 400 ml beaker, 80 percent full of boiling water, for 10 minutes. Enough heat must be supplied to prevent the water bath from cooling much below the boiling point upon inserting the volumetric flask. Remove the flask, cool to room temperature, dilute to the mark, and mix.

11.2.2 Transfer a suitable portion of the reference solution to an absorption cell, and adjust the spectrophotometer to the initial setting using a light band centered at 660 nm. While maintaining this spectrophotometer adjustment, take the readings of the calibration solutions followed by the samples.

11.3 Audit Sample Analysis. Same as in Method 108A, Section 11.6.

12.0 Data Analysis and Calculations

Same as in Method 108A, Section 12.0.

13.0 Method Performance. [Reserved]

14.0 Pollution Prevention. [Reserved]

15.0 Waste Management. [Reserved]

16.0 References

1. Ringwald, D. Arsenic Determination on Process Materials from ASARCO's Copper Smelter in Tacoma, Washington. Unpublished Report. Prepared for the Emission Measurement Branch, Technical Support Division, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina. August 1980. 35 pp.

BILLING CODE 6560-50-P

17.0 Tables, Diagrams, Flowcharts, and Validation Data

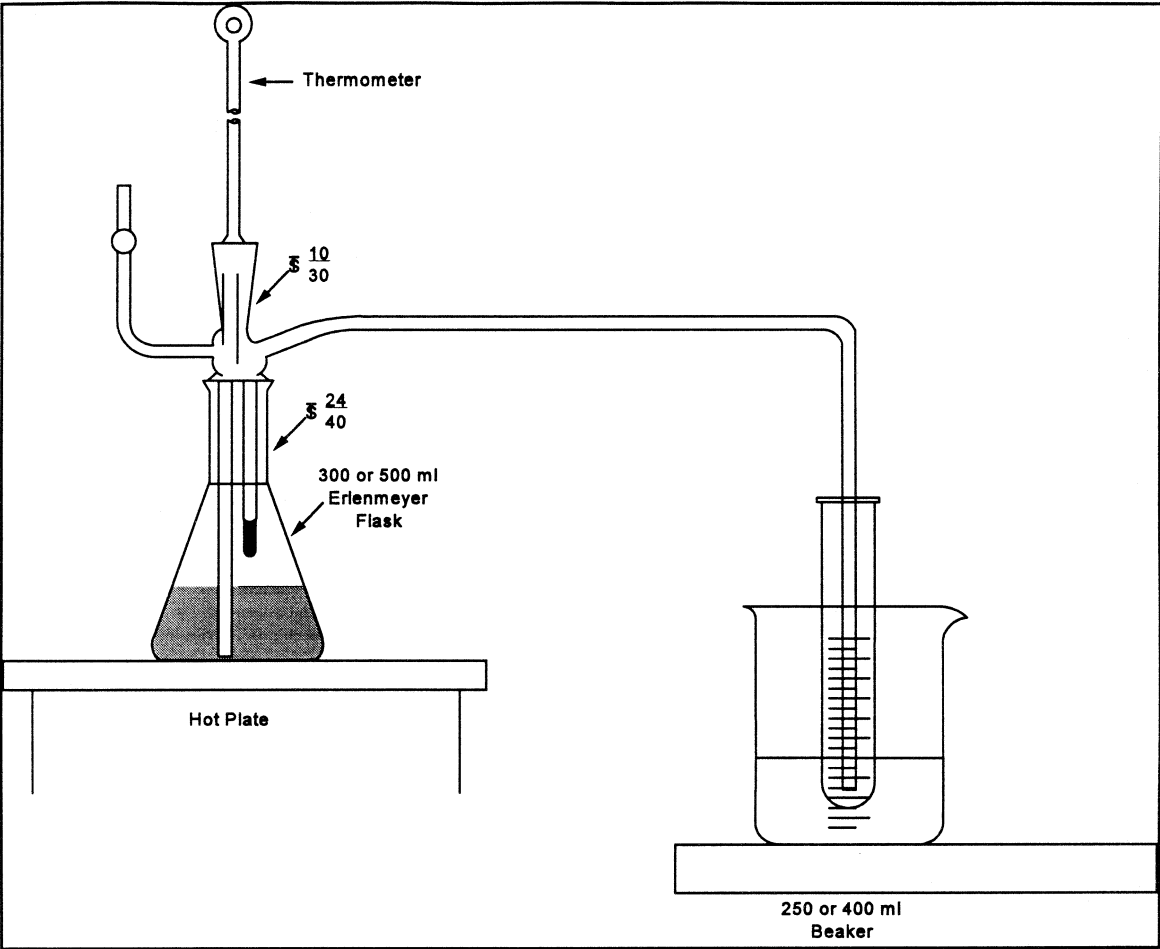


Figure 108C-1. Distillation Apparatus.

BILLING CODE 6560-50-C

Method 111—Determination of Polonium-210 Emissions From Stationary Sources

NOTE: This method does not include all of the specifications (e.g., equipment and supplies) and procedures (e.g., sampling and analytical) essential to its performance. Some material is incorporated by reference from methods in appendix A to 40 CFR Part 60. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 2, Method 3, and Method 5.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Polonium	7440-08-6	Not specified.

1.2 Applicability. This method is applicable for the determination of the polonium-210 content of particulate matter samples collected from stationary source exhaust stacks, and for the use of these data to calculate polonium-210 emissions from individual sources and from all affected sources at a facility.

1.3 Data Quality Objectives. Adherence to the requirements of this

method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

A particulate matter sample, collected according to Method 5, is analyzed for polonium-210 content: the polonium-210 in the sample is put in solution, deposited on a metal disc, and the

radioactive disintegration rate measured. Polonium in acid solution spontaneously deposits on surfaces of metals that are more electropositive than polonium. This principle is routinely used in the radiochemical analysis of polonium-210. Data reduction procedures are provided, allowing the calculation of polonium-210 emissions from individual sources

and from all affected sources at a facility, using data obtained from Methods 2 and 5 and from the analytical procedures herein.

3.0 Definitions [Reserved]

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive Reagents. The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burns as thermal burns.

5.2.1 Hydrochloric Acid (HCl). Highly corrosive liquid with toxic vapors. Vapors are highly irritating to eyes, skin, nose, and lungs, causing severe damage. May cause bronchitis, pneumonia, or edema of lungs. Exposure to concentrations of 0.13 to 0.2 percent can be lethal to humans in a few minutes. Provide ventilation to limit exposure. Reacts with metals, producing hydrogen gas.

5.2.2 Hydrofluoric Acid (HF). Highly corrosive to eyes, skin, nose, throat, and lungs. Reaction to exposure may be delayed by 24 hours or more. Provide ventilation to limit exposure.

5.2.3 Nitric Acid (HNO₃). Highly corrosive to eyes, skin, nose, and lungs. Vapors cause bronchitis, pneumonia, or edema of lungs. Reaction to inhalation may be delayed as long as 30 hours and still be fatal. Provide ventilation to limit exposure. Strong oxidizer. Hazardous

reaction may occur with organic materials such as solvents.

5.2.4 Perchloric Acid (HClO₄). Corrosive to eyes, skin, nose, and throat. Provide ventilation to limit exposure. Keep separate from water and oxidizable materials to prevent vigorous evolution of heat, spontaneous combustion, or explosion. Heat solutions containing HClO₄ only in hoods specifically designed for HClO₄.

6.0 Equipment and Supplies

6.1 Alpha Spectrometry System. Consisting of a multichannel analyzer, biasing electronics, silicon surface barrier detector, vacuum pump and chamber.

6.2 Constant Temperature Bath at 85 °C (185 °F).

6.3 Polished Silver Discs. 3.8 cm diameter, 0.4 mm thick with a small hole near the edge.

6.4 Glass Beakers. 400 ml, 150 ml.

6.5 Hot Plate, Electric.

6.6 Fume Hood.

6.7 Teflon Beakers, 150 ml.

6.8 Magnetic Stirrer.

6.9 Stirring Bar.

6.10 Hooks. Plastic or glass, to suspend plating discs.

6.11 Internal Proportional Counter. For measuring alpha particles.

6.12 Nucleopore Filter Membranes. 25 mm diameter, 0.2 micrometer pore size or equivalent.

6.13 Planchets. Stainless steel, 32 mm diameter with 1.5 mm lip.

6.14 Transparent Plastic Tape. 2.5 cm wide with adhesive on both sides.

6.15 Epoxy Spray Enamel.

6.16 Suction Filter Apparatus. For 25 mm diameter filter.

6.17 Wash Bottles, 250 ml capacity.

6.18 Graduated Cylinder, plastic, 25 ml capacity.

6.19 Volumetric Flasks, 100 ml, 250 ml.

7.0 Reagents and Standards

Unless otherwise indicated, it is intended that all reagents conform to the

specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available; otherwise, use the best available grade.

7.1 Ascorbic Acid.

7.2 Ammonium Hydroxide (NH₄OH), 15 M.

7.3 Water. Deionized distilled, to conform to ASTM D 1193-77 or 91 (incorporated by reference—see § 61.18), Type 3. Use in all dilutions requiring water.

7.4 Ethanol (C₂H₅OH), 95 percent.

7.5 Hydrochloric Acid, 12 M.

7.6 Hydrochloric Acid, 1 M. Dilute 83 ml of the 12 M HCl to 1 liter with distilled water.

7.7 Hydrofluoric Acid, 29 M.

7.8 Hydrofluoric Acid, 3 M. Dilute 52 ml of the 29 M HF to 500 ml with distilled water. Use a plastic graduated cylinder and storage bottle.

7.9 Lanthanum Carrier, 0.1 mg La⁺³/ml. Dissolve 0.078 gram lanthanum nitrate, La(NO₃)₃·6H₂O in 250 ml of 1 M HCl.

7.10 Nitric Acid, 16 M.

7.11 Perchloric Acid, 12 M.

7.12 Polonium-209 Solution.

7.13 Silver Cleaner. Any mild abrasive commercial silver cleaner.

7.14 Degreaser.

7.15 Standard Solution.

Standardized solution of an alpha-emitting actinide element, such as plutonium-239 or americium-241.

8.0 Sample Collection, Preservation, Transport, and Storage. [Reserved]

9.0 Quality Control

9.1 General Requirement.

9.1.1 All analysts using this method are required to demonstrate their ability to use the method and to define their respective accuracy and precision criteria.

9.2 Miscellaneous Quality Control Measures.

Section	Quality control measure	Effect
10.1	Standardization of alpha spectrometry system	Ensure precision of sample analyses.
10.3	Standardization of internal proportional counter.	Ensure precise sizing of sample aliquot.
11.1, 11.2	Determination of procedure background and instrument background.	Minimize background effects.
11.3	Audit sample analysis	Evaluate analyst's technique.

10.0 Calibration and Standardization

10.1 Standardization of Alpha Spectrometry System.

10.1.1 Add a quantity of the actinide standard solution to a 100 ml volumetric flask so that the final

concentration when diluted to a volume of 100 ml will be approximately 1 pCi/ml.

10.1.2 Add 10 ml of 16 M HNO₃ and dilute to 100 ml with water.

10.1.3 Add 20 ml of 1 M HCl to each of six 150 ml beakers. Add 1.0 ml of

lanthanum carrier, 0.1 mg lanthanum per ml, to the acid solution in each beaker.

10.1.4 Add 1.0 ml of the 1 pCi/ml working solution (from Section 10.1.1)

to each beaker. Add 5.0 ml of 3 M HF to each beaker.

10.1.5 Cover beakers and allow solutions to stand for a minimum of 30 minutes. Filter the contents of each beaker through a separate filter membrane using the suction filter apparatus. After each filtration, wash the filter membrane with 10 ml of distilled water and 5 ml of ethanol, and allow the filter membrane to air dry on the filter apparatus.

10.1.6 Carefully remove the filter membrane and mount it, filtration side up, with double-side tape on the inner surface of a planchet. Place planchet in an alpha spectrometry system and count each planchet for 1000 minutes.

10.1.7 Calculate the counting efficiency of the detector for each aliquot of the 1 pCi/ml actinide working solution using Eq. 111-1 in Section 12.2.

10.1.8 Determine the average counting efficiency of the detector, E_c , by calculating the average of the six determinations.

10.2 Preparation of Standardized Solution of Polonium-209.

10.2.1 Add a quantity of the Po-209 solution to a 100 ml volumetric flask so that the final concentration when diluted to a 100 ml volume will be approximately 1 pCi/ml.

10.2.2 Follow the procedures outlined in Sections 10.1.2 through 10.1.6, except substitute 1.0 ml of polonium-209 tracer solution (Section 10.2.1) and 3.0 ml of 15 M ammonium hydroxide for the 1 pCi/ml actinide working solution and the 3 M HF, respectively.

10.2.3 Calculate the activity of each aliquot of the polonium-209 tracer solution using Eq. 111-2 in Section 12.3.

10.2.4 Determine the average activity of the polonium-209 tracer solution, F , by averaging the results of the six determinations.

10.3 Standardization of Internal Proportional Counter

10.3.1 Add a quantity of the actinide standard solution to a 100 ml volumetric flask so that the final concentration when diluted to a 100 ml volume will be approximately 100 pCi/ml.

10.3.2 Follow the procedures outlined in Sections 10.1.2 through 10.1.6, except substitute the 100 pCi/ml actinide working solution for the 1 pCi/ml solution, place the planchet in an internal proportional counter (instead of an alpha spectrometry system), and count for 100 minutes (instead of 1000 minutes).

10.3.3 Calculate the counting efficiency of the internal proportional

counter for each aliquot of the 100 pCi/ml actinide working solution using Eq. 111-3 in 12.4.

10.3.4 Determine the average counting efficiency of the internal proportional counter, E_i , by averaging the results of the six determinations.

11.0 Analytical Procedure

Note: Perform duplicate analyses of all samples, including background counts, quality assurance audit samples, and Method 5 samples. Duplicate measurements are considered acceptable when the difference between them is less than two standard deviations as described in EPA 600/4-77-001 or subsequent revisions.

11.1 Determination of Procedure Background. Background counts used in all equations are determined by performing the specific analysis required using the analytical reagents only. All procedure background counts and sample counts for the internal proportional counter should utilize a counting time of 100 minutes; for the alpha spectrometry system, 1000 minutes. These background counts should be performed no less frequently than once per 10 sample analyses.

11.2 Determination of Instrument Background. Instrument backgrounds of the internal proportional counter and the alpha spectrometry system should be determined on a weekly basis. Instrument background should not exceed procedure background. If this occurs, it may be due to a malfunction or contamination, and should be corrected before use.

11.3 Quality Assurance Audit Samples. An externally prepared performance evaluation sample shall be analyzed no less frequently than once per 10 sample analyses, and the results reported with the test results.

11.4 Sample Preparation. Treat the Method 5 samples [i.e., the glass fiber filter (Container No. 1) and the acetone rinse (Container No. 2)] as follows:

11.4.1 Container No. 1. Transfer the filter and any loose particulate matter from the sample container to a 150-ml Teflon beaker.

11.4.2 Container No. 2. Note the level of liquid in the container, and confirm on the analysis sheet whether leakage occurred during transport. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results. Transfer the contents to a 400-ml glass beaker. Add polonium-209 tracer solution to the glass beaker in an amount approximately equal to the amount of polonium-210 expected in the total particulate sample. Record the activity of the tracer solution added.

Add 16 M nitric acid to the beaker to digest and loosen the residue.

11.4.3 Transfer the contents of the glass beaker to the Teflon beaker containing the glass fiber filter. Rinse the glass beaker with 16 M HNO_3 . If necessary, reduce the volume in the beaker by evaporation until all of the nitric acid HNO_3 from the glass beaker has been transferred to the Teflon beaker.

11.4.4 Add 30 ml of 29 M HF to the Teflon beaker and evaporate to near dryness on a hot plate in a properly operating hood.

Note: Do not allow the residue to go to dryness and overheat; this will result in loss of polonium.

11.4.5 Repeat step 11.4.4 until the filter is dissolved.

11.4.6 Add 100 ml of 16 M HNO_3 to the residue in the Teflon beaker and evaporate to near dryness.

Note: Do not allow the residue to go to dryness.

11.4.7 Add 50 ml of 16 M HNO_3 and 10 ml of 12 M perchloric acid to the Teflon beaker and heat until dense fumes of perchloric acid are evolved.

11.4.8 Repeat steps 11.4.4 to 11.4.7 as necessary until sample is completely dissolved.

11.4.9 Add 10 ml of 12 M HCl to the Teflon beaker and evaporate to dryness. Repeat additions and evaporations several times.

11.4.10 Transfer the sample to a 250-ml volumetric flask and dilute to volume with 3 M HCl.

11.5 Sample Screening. To avoid contamination of the alpha spectrometry system, check each sample as follows:

11.5.1 Add 20 ml of 1 M HCl, 1 ml of the lanthanum carrier solution (0.1 mg La/ml), a 1 ml aliquot of the sample solution from Section 11.4.10, and 3 ml of 15 M ammonium hydroxide to a 250-ml beaker in the order listed. Allow this solution to stand for a minimum of 30 minutes.

11.5.2 Filter the solution through a filter membrane using the suction filter apparatus. Wash the filter membrane with 10 ml of water and 5 ml of ethanol, and allow the filter membrane to air dry on the filter apparatus.

11.5.3 Carefully remove the filter membrane and mount it, filtration side up, with double-side tape on the inner surface of a planchet. Place the planchet in an internal proportional counter, and count for 100 minutes.

11.5.4 Calculate the activity of the sample using Eq. 111-4 in Section 12.5.

11.5.5 Determine the aliquot volume of the sample solution from Section 11.4.10 to be analyzed for polonium-210, such that the aliquot contains an

activity between 1 and 4 picocuries. Use Eq. 111-5 in Section 12.6.

11.6 Preparation of Silver Disc for Spontaneous Electrodeposition.

11.6.1 Clean both sides of the polished silver disc with silver cleaner and with degreaser.

11.6.2 Place disc on absorbent paper and spray one side with epoxy spray enamel. This should be carried out in a well-ventilated area, with the disc lying flat to keep paint on one side only. Allow paint to dry for 24 hours before using disc for deposition.

11.7 Sample Analysis.

11.7.1 Add the aliquot of sample solution from Section 11.4.10 to be analyzed for polonium-210, the volume of which was determined in Section 11.5.5, to a suitable 200-ml container to be placed in a constant temperature bath.

Note: Aliquot volume may require a larger container.

11.7.2 If necessary, bring the volume to 100 ml with 1 M HCl. If the aliquot volume exceeds 100 ml, use total aliquot.

11.7.3 Add 200 mg of ascorbic acid and heat solution to 85 °C (185 °F) in a constant temperature bath.

11.7.4 Suspend a silver disc in the heated solution using a glass or plastic rod with a hook inserted through the hole in the disc. The disc should be totally immersed in the solution, and the solution must be stirred constantly, at all times during the plating operation. Maintain the disc in solution for 3 hours.

11.7.5 Remove the silver disc, rinse with deionized distilled water, and allow to air dry at room temperature.

11.7.6 Place the disc, with deposition side (unpainted side) up, on a planchet and secure with double-side plastic tape. Place the planchet with disc in alpha spectrometry system and count for 1000 minutes.

12.0 Data Analysis and Calculations.

12.1 Nomenclature.

A = Picocuries of polonium-210 in the Method 5 sample (from Section 12.8).

A_A = Picocuries of actinide added.

A_L = Volume of sample aliquot used, in ml (specified in Section 11.5.1 as 1 ml).

A_S = Aliquot to be analyzed, in ml.

B_B = Procedure background counts measured in polonium-209 spectral region.

B_T = Polonium-209 tracer counts in sample.

C_T = Total counts in polonium-210 spectral region.

D = Decay correction for time "t" (in days) from sample collection to sample counting, given by:
 $D = e^{-0.005t}$

E_C = Average counting efficiency of detector (from Section 10.1.8), as counts per disintegration.

E_{Ci} = Counting efficiency of the detector for aliquot i of the actinide working solution, counts per disintegration.

E_I = Average counting efficiency of the internal proportional counter, as determined in Section 10.3.4, counts per disintegration.

E_{Ii} = Counting efficiency of the internal proportional counter for aliquot i of the 100 pCi/ml actinide working solution, counts per disintegration.

E_Y = The fraction of polonium-209 recovered on the planchet (from Section 12.7).

F = Average activity of polonium-209 in sample (from Section 10.2.4), in pCi.

F_i = activity of aliquot i of the polonium-209 tracer solution, in pCi.

L = Dilution factor (unitless). This is the volume of sample solution prepared (specified as 250 ml in Section 11.1.10) divided by the volume of the aliquot of sample solution analyzed for polonium-210 (from Section 11.7.1).

M_i = Phosphorous rock processing rate of the source being tested, during run i, Mg/hr.

M_k = Phosphate rock processed annually by source k, in Mg/yr.

n = Number of calciners at the elemental phosphorus plant.

P = Total activity of sample solution from Section 11.4.10, in pCi (see Eq. 111-4).

Q_{sd} = Volumetric flow rate of effluent stream, as determined by Method 2, in dscm/hr.

S = Annual polonium-210 emissions from the entire facility, in curies/yr.

V_{m(std)} = Volume of air sample, as determined by Method 5, in dscm.

X_k = Emission rate from source k, from Section 12.10, in curies/Mg.

10⁻¹² = Curies per picocurie.

2.22 = Disintegrations per minute per picocurie.

250 = Volume of solution from Section 11.4.10, in ml.

12.2 Counting Efficiency. Calculate the counting efficiency of the detector for each aliquot of the 1 pCi/ml actinide working solution using Eq. 111-1.

$$E_{Ci} = \frac{C_S - C_B}{2.22 A_A T} \quad \text{Eq. 111-1}$$

Where:

C_B = Background counts in same peak area as C_S.

C_S = Gross counts in actinide peak.

T = Counting time in minutes, specified in Section 10.1.6 as 1000 minutes.

$$F_i = \frac{C_S - C_B}{2.22 E_{Ci} T} \quad \text{Eq. 111-2}$$

Where:

C_B = Background counts in the 4.88 MeV region of spectrum the in the counting time T.

C_S = Gross counts of polonium-209 in the 4.88 MeV region of the spectrum in the counting time T.

T = Counting time, specified in Section 10.1.6 as 1000 minutes.

12.3 Polonium-209 Tracer Solution Activity. Calculate the activity of each aliquot of the polonium-209 tracer solution using Eq. 111-2.

12.4 Control Efficiency of Internal Proportional Counter. Calculate the counting efficiency of the internal proportional counter for each aliquot of the 100 pCi/ml actinide working solution using Eq. 111-3.

$$E_{li} = \frac{C_S - C_B}{2.22 A_A T} \quad \text{Eq. 111-3}$$

Where:

C_B = Gross counts of procedure background.

C_S = Gross counts of standard.

T = Counting time in minutes, specified in Section 10.3.2 as 100 minutes.

12.5 Calculate the activity of the sample using Eq. 111-4.

$$P = \frac{250 (C_S - C_B)}{2.22 \bar{E}_I A_L T} \quad \text{Eq. 111-4}$$

Where:

C_B = Total counts of procedure background. (See Section 11.1).

C_S = Total counts of screening sample.

T = Counting time for sample and background (which must be equal), in minutes (specified in Section 11.5.3 as 100 minutes).

12.6 Aliquot Volume. Determine the aliquot volume of the sample solution from Section 11.4.10 to be analyzed for polonium-210, such that the aliquot contains an activity between 1 and 4 picocuries using Eq. 111-5.

$$A_s = \frac{250 (\text{desired picocuries in aliquot})}{P} \quad \text{Eq. 111-5}$$

12.7 Polonium-209 Recovery. Calculate the fraction of polonium-209

recovered on the planchet, E_Y , using Eq. 111-6.

$$E_Y = \frac{B_T - B_B}{2.22 \bar{F} \bar{E}_C T} \quad \text{Eq. 111-6}$$

Where:

T = Counting time, specified in Section 11.1 as 1000 minutes.

12.8 Polonium-210 Activity.

Calculate the activity of polonium-210 in the Method 5 sample (including glass

fiber filter and acetone rinse) using Eq. 111-7.

$$A = \frac{(C_T - C_B) L}{2.22 E_Y \bar{E}_C T D} \quad \text{Eq. 111-7}$$

Where:

C_B = Procedure background counts in polonium-210 spectral region.

T = Counting time, specified in Section 11.1 as 1000 minutes for all alpha spectrometry sample and background counts.

12.9 Emission Rate from Each Stack.

12.9.1 For each test run, i , on a stack, calculate the measured polonium-210 emission rate, R_{Si} , using Eq. 111-8.

$$R_{Si} = \frac{(10^{-12}) A Q_{sd}}{V_{m(std)} M_i} \quad \text{Eq. 111-8}$$

12.9.2 Determine the average polonium-210 emission rate from the stack, R_s , by taking the sum of the measured emission rates for all runs, and dividing by the number of runs performed.

12.9.3 Repeat steps 12.9.1 and 12.9.2 for each stack of each calciner.

12.10 Emission Rate from Each Source. Determine the total polonium-210 emission rate, X_k , from each source, k , by taking the sum of the average

emission rates from all stacks to which the source exhausts.

12.11 Annual Polonium-210 Emission Rate from Entire Facility. Determine the annual elemental phosphorus plant emissions of polonium-210, S , using Eq. 111-9.

$$S = \frac{\sum_{k=1}^n (X_k M_k)}{n} \quad \text{Eq. 111-9}$$

13.0 Method Performance. [Reserved]**14.0 Pollution Prevention. [Reserved]****15.0 Waste Management. [Reserved]****16.0 References**

1. Blanchard, R.L. "Rapid Determination of Lead-210 and Polonium-210 in Environmental Samples by Deposition on Nickel." *Anal. Chem.*, 38:189, pp. 189–192. February 1966.

17.0 Tables, Diagrams, Flowcharts, and Validation Data [Reserved]

* * * * *

PART 63—NATIONAL EMISSION STANDARDS FOR HAZARDOUS AIR POLLUTANTS FOR SOURCE CATEGORIES

1. The authority citation for Part 63 continues to read as follows:

Authority: 42 U.S.C. 7401 *et seq.*

§ 63.7 [Amended]

2. Amend § 63.7 by revising paragraph (c)(4)(i) as follows:

§ 63.7 Performance testing requirements.

* * * * *

(c) * * *

(4)(i) Performance test method audit program. The owner or operator shall analyze performance audit (PA) samples during each performance test. The owner or operator shall request performance audit materials 45 days prior to the test date. Cylinder audit gases, if available, must be obtained from the appropriate EPA Regional Office or from the responsible enforcement authority and analyzed in conjunction with the field samples.

* * * * *

§ 63.11 [Amended]

3. Amend § 63.11 as follows:

a. The definition of "C_i" in paragraph (b)(6)(ii) is amended by revising "D1946-77" to read "D1946-77 or 90 (Reapproved 1994)."

b. The definition of "H_i" in paragraph (b)(6)(ii) is amended by revising "D2382-76" to read "D2382-76 or 88 or D4809-95."

§ 63.14 [Amended]

4. In § 63.14, by revising paragraph (b) to read as follows:

§ 63.14 Incorporation by reference.

* * * * *

(b) The following materials are available for purchase from at least one of the following addresses: American Society for Testing and Materials (ASTM), 1916 Race Street, Philadelphia, PA 19103; or University Microfilms

International, 300 North Zeeb Road, Ann Arbor, MI 48106.

(1) ASTM D523-89, Standard Test Method for Specular Gloss, IBR approved for § 63.782.

(2) ASTM D1193-77, 91, Standard Specification for Reagent Water, IBR approved for Appendix A: Method 306, Sections 7.1.1 and 7.4.2.

(3) ASTM D1331-89, Standard Test Methods for Surface and Interfacial Tension of Solutions of Surface Active Agents, IBR approved for Appendix A: Method 306B, Sections 6.2, 11.1, and 12.2.2.

(4) ASTM D1475-90, Standard Test Method for Density of Paint, Varnish Lacquer, and Related Products, IBR approved for § 63.788, Appendix A.

(5) ASTM D1946-77, 90, 94, Standard Method for Analysis of Reformed Gas by Gas Chromatography, IBR approved for § 63.11(b)(6).

(6) ASTM D2369-93, 95, Standard Test Method for Volatile Content of Coatings, IBR approved for § 63.788, Appendix A.

(7) ASTM D2382-76, 88, Heat of Combustion of Hydrocarbon Fuels by Bomb Calorimeter (High-Precision Method), IBR approved for § 63.11(b)(6).

(8) ASTM D2879-83, 96, Test Method for Vapor Pressure-Temperature Relationship and Initial Decomposition Temperature of Liquids by Isoteniscope, IBR approved for § 63.111 of Subpart G.

(9) ASTM D3257-93, Standard Test Methods for Aromatics in Mineral Spirits by Gas Chromatography, IBR approved for § 63.786(b).

(10) ASTM 3695-88, Standard Test Method for Volatile Alcohols in Water by Direct Aqueous-Injection Gas Chromatography, IBR approved for § 63.365(e)(1) of Subpart O.

(11) ASTM D3792-91, Standard Method for Water Content of Water-Reducible Paints by Direct Injection into a Gas Chromatograph, IBR approved for § 63.788, Appendix A.

(12) ASTM D3912-80, Standard Test Method for Chemical Resistance of Coatings Used in Light-Water Nuclear Power Plants, IBR approved for § 63.782.

(13) ASTM D4017-90, 96a, Standard Test Method for Water in Paints and Paint Materials by the Karl Fischer Titration Method, IBR approved for § 63.788, Appendix A.

(14) ASTM D4082-89, Standard Test Method for Effects of Gamma Radiation on Coatings for Use in Light-Water Nuclear Power Plants, IBR approved for § 63.782.

(15) ASTM D4256-89, 94, Standard Test Method for Determination of the Decontaminability of Coatings Used in

Light-Water Nuclear Power Plants, IBR approved for § 63.782.

(16) ASTM D4809-95, Standard Test Method for Heat of Combustion of Liquid Hydrocarbon Fuels by Bomb Calorimeter (Precision Method), IBR approved for § 63.11(b)(6).

(17) ASTM E180-93, Standard Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial Chemicals, IBR approved for § 63.786(b).

(18) ASTM E260-91, 96, General Practice for Packed Column Gas Chromatography, IBR approved for §§ 63.750(b)(2) and 63.786(b)(5).

§ 63.111 [Amended]

5. In § 63.111, paragraph (3) of the definition of the term "Maximum true vapor pressure" is amended by revising "D2879-83" to read "D2879-83 or 96."

§ 63.301 [Amended]

6. Amend § 63.301 as follows:

a. The definition of the term "Foundry coke producer" is amended by revising the words "1.25 million megagrams per year" to read "1.25 million megagrams per year (1.38 million tons per year)."

b. The definitions of the terms "Short coke oven battery" and "Tall coke oven battery" are amended by revising the words "6 meters" to read "6 meters (20 feet)" wherever they occur.

§ 63.304 [Amended]

7. In § 63.304, paragraph (b)(6)(iii) is amended by revising the words "2.7 million Mg/yr" to read "2.7 million Mg/yr (3.0 million ton/yr)."

§ 63.750 [Amended]

8. In § 63.750, paragraph (b)(2) is amended by revising "ASTM E 260-91 (incorporated by reference as specified in § 63.14 of subpart A of this part)" to read "ASTM E 260-91 or 96 (incorporated by reference—see § 63.14 of Subpart A of this part)."

§ 63.782 [Amended]

9. Amend § 63.782 as follows:

a. The definition for "High-gloss specialty coating" is amended by revising "ASTM Method D523," to read "ASTM D523-89."

b. The definition for Nuclear specialty coating is amended by revising "ASTM D4256-89," to read "ASTM D4256-89 or 94."

§ 63.786 [Amended]

10. In § 63.786, paragraph (b)(5) is amended by revising "ASTM Method E260-91" to read "ASTM E260-91 or 96."

§ 63.788 [Amended]

11. In § 63.788, the Appendix A to Subpart II of Part 63—VOC Data Sheet is amended by revising “ASTM Method D2369-93,” and “ASTM D4017-90” to read “ASTM D2369-93 or 95” and “ASTM D4017-81, 90, or 96a” respectively.

Appendix A—[Amended]

12. Amend Method 310B in Appendix A as follows:

a. Section 1.0 is amended by revising “ethylidene norbornene (ENB)” to read “Applicable Termonomer.”

b. Section 1.0 is amended by deleting “16219-75-3.”

c. In Section 5.0, correcting the section numbering from “5.1, 5.2, 5.3, 5.3, 5.4, 5.5, 5.6, and 5.7” to “5.1, 5.2, 5.3, 5.4, 5.5, 5.6, 5.7, and 5.8.”

d. Sections 5.3, 7.1, 7.2, 7.3, 7.5.6, 7.6, 7.6.1, 9.2, 10.1, 10.2.2, 10.2.5, 10.2.8, 12.3, and 12.6 are amended by revising “ENB” to read “termonomer” wherever it appears.

e. Sections 6.11, 7.5.1, 9.3.3, 11.1.2, and 12.5 are revised.

f. The first sentence in Section 7.1 is amended by revising to read “Reagent toluene, EM Science Omnisolv (or equivalent).”

g. Section 7.2 is amended by revising the first sentence to read “Reagent acetone, EM Science Omnisolv HR-GC (or equivalent).”

h. Section 7.3 is amended by revising the first sentence to read “Reagent heptane, Aldrich Chemical Gold Label, Cat #15,487-3 (or equivalent).”

i. Section 7.4.5 is amended by revising “Section 5.4.4” to read “7.4.4.”

j. Section 9.3 is amended by revising the first sentence to read “Recovery efficiency must be determined for high ethylene concentration, low ethylene concentration, E-P terpolymer, or oil extended samples and whenever modifications are made to the method.”

k. Section 13.1 is amended by revising the last sentence to read “Note: These values are examples; each sample type, as specified in Section 9.3, must be tested for sample recovery.”

The revisions read as follows:

Method 310B—Determination of Residual Hexane Through Gas Chromatography

* * * * *

6.0 Equipment and Supplies * * *

6.11 Crimp-top sample vials and HP p/n 5181-1211 crimp caps, or screw-top autosampler vials and screw tops.

* * * * *

7.5.1 Preparation of Polymer Dissolving Solution. Fill a 4,000-ml

volumetric flask about ¾ full with toluene.

* * * * *

9.3.3 The precipitated polymer from the steps described above shall be redissolved using toluene as the solvent. No heptane shall be added to the sample in the second dissolving step. The toluene solvent and acetone precipitant shall be determined to be free of interfering compounds.

* * * * *

11.1.2 Place crumb sample in bottle: RLA-3: 10 g (gives a dry wt. of ~5.5 g).

* * * * *

12.5 After obtaining the final dry weight of polymer used (Section 11.1.10 of this method), record that result in a “dry wt.” column of the logbook (for oil extended polymer, the amount of oil extracted is added to the dry rubber weight).

* * * * *

13. Appendix A to Part 63 is amended by revising Methods 303, 303A, 304A, 304B, 305, 306, 306A, and 306B to read as follows:

Method 303—Determination of Visible Emissions From By-Product Coke Oven Batteries

Note: This method is not inclusive with respect to observer certification. Some material is incorporated by reference from other methods in appendix A to 40 CFR part 60. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of Method 9.

1.0 Scope and Application

1.1 Applicability. This method is applicable for the determination of visible emissions (VE) from the following by-product coke oven battery sources: charging systems during charging; doors, topside port lids, and offtake systems on operating coke ovens; and collecting mains. This method is also applicable for qualifying observers for visually determining the presence of VE.

2.0 Summary of Method

2.1 A certified observer visually determines the VE from coke oven battery sources. Certification procedures are presented. This method does not require that opacity of emissions be determined or that magnitude be differentiated.

3.0 Definitions

3.1 *Bench* means the platform structure in front of the oven doors.

3.2 *By-product Coke Oven Battery* means a source consisting of a group of ovens connected by common walls, where coal undergoes destructive

distillation under positive pressure to produce coke and coke oven gas, from which by-products are recovered.

3.3 *Charge or charging period* means the period of time that commences when coal begins to flow into an oven through a topside port and ends when the last charging port is recapped.

3.4 *Charging system* means an apparatus used to charge coal to a coke oven (e.g., a larry car for wet coal charging systems).

3.5 *Coke oven door* means each end enclosure on the push side and the coking side of an oven. The chuck, or leveler-bar, door is considered part of the push side door. The coke oven door area includes the entire area on the vertical face of a coke oven between the bench and the top of the battery between two adjacent buck stays.

3.6 *Coke side* means the side of a battery from which the coke is discharged from ovens at the end of the coking cycle.

3.7 *Collecting main* means any apparatus that is connected to one or more offtake systems and that provides a passage for conveying gases under positive pressure from the by-product coke oven battery to the by-product recovery system.

3.8 *Consecutive charges* means charges observed successively, excluding any charge during which the observer's view of the charging system or topside ports is obscured.

3.9 *Damper-off* means to close off the gas passage between the coke oven and the collecting main, with no flow of raw coke oven gas from the collecting main into the oven or into the oven's offtake system(s).

3.10 *Decarbonization period* means the period of time for combusting oven carbon that commences when the oven lids are removed from an empty oven or when standpipe caps of an oven are opened. The period ends with the initiation of the next charging period for that oven.

3.11 *Larry car* means an apparatus used to charge coal to a coke oven with a wet coal charging system.

3.12 *Log average* means logarithmic average as calculated in Section 12.4.

3.13 *Offtake system* means any individual oven apparatus that is stationary and provides a passage for gases from an oven to a coke oven battery collecting main or to another oven. Offtake system components include the standpipe and standpipe caps, goosenecks, stationary jumper pipes, mini-standpipes, and standpipe and gooseneck connections.

3.14 *Operating oven* means any oven not out of operation for rebuild or maintenance work extensive enough to

require the oven to be skipped in the charging sequence.

3.15 *Oven* means a chamber in the coke oven battery in which coal undergoes destructive distillation to produce coke.

3.16 *Push side* means the side of the battery from which the coke is pushed from ovens at the end of the coking cycle.

3.17 *Run* means the observation of visible emissions from topside port lids, offtake systems, coke oven doors, or the charging of a single oven in accordance with this method.

3.18 *Shed* means an enclosure that covers the side of the coke oven battery, captures emissions from pushing operations and from leaking coke oven doors on the coke side or push side of the coke oven battery, and routes the emissions to a control device or system.

3.19 *Standpipe cap* means An apparatus used to cover the opening in the gooseneck of an offtake system.

3.20 *Topside port lid* means a cover, removed during charging or decarbonizing, that is placed over the opening through which coal can be charged into the oven of a by-product coke oven battery.

3.21 *Traverse time* means accumulated time for a traverse as measured by a stopwatch. Traverse time includes time to stop and write down oven numbers but excludes time waiting for obstructions of view to clear or for time to walk around obstacles.

3.22 *Visible Emissions or VE* means any emission seen by the unaided (except for corrective lenses) eye, excluding steam or condensing water.

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

5.2 Safety Training. Because coke oven batteries have hazardous environments, the training materials and the field training (Section 10.0) shall cover the precautions required by the company to address health and safety hazards. Special emphasis shall be given to the Occupational Safety and Health Administration (OSHA) regulations pertaining to exposure of coke oven workers (see Reference 3 in Section 16.0). In general, the regulation requires that special fire-retardant

clothing and respirators be worn in certain restricted areas of the coke oven battery. The OSHA regulation also prohibits certain activities, such as chewing gum, smoking, and eating in these areas.

6.0 Equipment and Supplies [Reserved]

7.0 Reagents and Standards [Reserved]

8.0 Sample Collection, Preservation, Transport, and Storage [Reserved]

9.0 Quality Control [Reserved]

10.0 Calibration and Standardization

Observer certification and training requirements are as follows:

10.1 Certification Procedures. This method requires only the determination of whether VE occur and does not require the determination of opacity levels; therefore, observer certification according to Method 9 in appendix A to part 60 of this chapter is not required to obtain certification under this method. However, in order to receive Method 303 observer certification, the first-time observer (trainee) shall have attended the lecture portion of the Method 9 certification course. In addition, the trainee shall successfully complete the Method 303 training course, satisfy the field observation requirement, and demonstrate adequate performance and sufficient knowledge of Method 303. The Method 303 training course shall be conducted by or under the sanction of the EPA and shall consist of classroom instruction and field observations, and a proficiency test.

10.1.1 The classroom instruction shall familiarize the trainees with Method 303 through lecture, written training materials, and a Method 303 demonstration video. A successful completion of the classroom portion of the Method 303 training course shall be demonstrated by a perfect score on a written test. If the trainee fails to answer all of the questions correctly, the trainee may review the appropriate portion of the training materials and retake the test.

10.1.2 The field observations shall be a minimum of 12 hours and shall be completed before attending the Method 303 certification course. Trainees shall observe the operation of a coke oven battery as it pertains to Method 303, including topside operations, and shall also practice conducting Method 303 or similar methods. During the field observations, trainees unfamiliar with coke battery operations shall receive instruction from an experienced coke oven observer familiar with Method 303 or similar methods and with the operation of coke batteries. The trainee

must verify completion of at least 12 hours of field observation prior to attending the Method 303 certification course.

10.1.3 All trainees must demonstrate proficiency in the application of Method 303 to a panel of three certified Method 303 observers, including an ability to differentiate coke oven emissions from condensing water vapor and smoldering coal. Each panel member shall have at least 120 days experience in reading visible emissions from coke ovens. The visible emissions inspections that will satisfy the experience requirement must be inspections of coke oven battery fugitive emissions from the emission points subject to emission standards under subpart L of this part (*i.e.*, coke oven doors, topside port lids, offtake system(s), and charging operations), using either Method 303 or predecessor State or local test methods. A "day's experience" for a particular inspection is a day on which one complete inspection was performed for that emission point under Method 303 or a predecessor State or local method. A "day's experience" does not mean 8 or 10 hours performing inspections, or any particular time expressed in minutes or hours that may have been spent performing them. Thus, it would be possible for an individual to qualify as a Method 303 panel member for some emission points, but not others (*e.g.*, an individual might satisfy the experience requirement for coke oven doors, but not topside port lids). Until November 15, 1994, the EPA may waive the certification requirement (but not the experience requirement) for panel members. The composition of the panel shall be approved by the EPA. The panel shall observe the trainee in a series of training runs and a series of certification runs. There shall be a minimum of 1 training run for doors, topside port lids, and offtake systems, and a minimum of 5 training runs (*i.e.*, 5 charges) for charging. During training runs, the panel can advise the trainee on proper procedures. There shall be a minimum of 3 certification runs for doors, topside port lids, and offtake systems, and a minimum of 15 certification runs for charging (*i.e.*, 15 charges). The certifications runs shall be unassisted. Following the certification test runs, the panel shall approve or disapprove certification based on the trainee's performance during the certification runs. To obtain certification, the trainee shall demonstrate to the satisfaction of the panel a high degree of proficiency in performing Method 303. To aid in evaluating the trainee's performance, a

checklist, provided by the EPA, will be used by the panel members.

10.2 **Observer Certification.** Recertification. The coke oven observer certification is valid for 1 year from date of issue. The observer shall recertify annually by viewing the training video and answering all of the questions on the certification test correctly. Every 3 years, an observer shall be required to pass the proficiency test in Section 10.1.3 in order to be certified.

10.3 The EPA (or applicable enforcement agency) shall maintain records reflecting a certified observer's successful completion of the proficiency test, which shall include the completed proficiency test checklists for the certification runs.

10.4 An owner or operator of a coke oven battery subject to subpart L of this part may observe a training and certification program under this section.

11.0 Procedure

11.1 **Procedure for Determining VE from Charging Systems During Charging.**

11.1.1 **Number of Oven Charges.** Refer to § 63.309(c)(1) of this part for the number of oven charges to observe. The observer shall observe consecutive charges. Charges that are nonconsecutive can only be observed when necessary to replace observations terminated prior to the completion of a charge because of visual interferences. (See Section 11.1.5).

11.1.2 **Data Records.** Record all the information requested at the top of the charging system inspection sheet (Figure 303-1). For each charge, record the identification number of the oven being charged, the approximate beginning time of the charge, and the identification of the larry car used for the charge.

11.1.3 **Observer Position.** Stand in an area or move to positions on the topside of the coke oven battery with an unobstructed view of the entire charging system. For wet coal charging systems or non-pipeline coal charging systems, the observer should have an unobstructed view of the emission points of the charging system, including larry car hoppers, drop sleeves, and the topside ports of the oven being charged. Some charging systems are configured so that all emission points can only be seen from a distance of five ovens. For other batteries, distances of 8 to 12 ovens are adequate.

11.1.4 **Observation.** The charging period begins when coal begins to flow into the oven and ends when the last charging port is recapped. During the charging period, observe all of the potential sources of VE from the entire

charging system. For wet coal charging systems or non-pipeline coal charging systems, sources of VE typically include the larry car hoppers, drop sleeves, slide gates, and topside ports on the oven being charged. Any VE from an open standpipe cap on the oven being charged is included as charging VE.

11.1.4.1 Using an accumulative-type stopwatch with unit divisions of at least 0.5 seconds, determine the total time VE are observed as follows. Upon observing any VE emerging from any part of the charging system, start the stopwatch. Stop the watch when VE are no longer observed emerging, and restart the watch when VE reemerges.

11.1.4.2 When VE occur simultaneously from several points during a charge, consider the sources as one. Time overlapping VE as continuous VE. Time single puffs of VE only for the time it takes for the puff to emerge from the charging system. Continue to time VE in this manner for the entire charging period. Record the accumulated time to the nearest 0.5 second under "Visible emissions, seconds" on Figure 303-1.

11.1.5 **Visual Interference.** If fugitive VE from other sources at the coke oven battery site (e.g., door leaks or condensing water vapor from the coke oven wharf) prevent a clear view of the charging system during a charge, stop the stopwatch and make an appropriate notation under "Comments" on Figure 303-1. Label the observation an observation of an incomplete charge, and observe another charge to fulfill the requirements of Section 11.1.1.

11.1.6 **VE Exemptions.** Do not time the following VE:

11.1.6.1 The VE from burning or smoldering coal spilled on top of the oven, topside port lid, or larry car surfaces;

Note: The VE from smoldering coal are generally white or gray. These VE generally have a plume of less than 1 meter long. If the observer cannot safely and with reasonable confidence determine that VE are from charging, do not count them as charging emissions.

11.1.6.2 The VE from the coke oven doors or from the leveler bar; or

11.1.6.3 The VE that drift from the top of a larry car hopper if the emissions had already been timed as VE from the drop sleeve.

Note: When the slide gate on a larry car hopper closes after the coal has been added to the oven, the seal may not be airtight. On occasions, a puff of smoke observed at the drop sleeves is forced past the slide gate up into the larry car hopper and may drift from the top; time these VE either at the drop sleeves or the hopper. If the larry car hopper does not have a slide gate or the slide gate is left open or partially closed, VE may

quickly pass through the larry car hopper without being observed at the drop sleeves and will appear as a strong surge of smoke; time these as charging VE.

11.1.7 **Total Time Record.** Record the total time that VE were observed for each charging operation in the appropriate column on the charging system inspection sheet.

11.1.8 **Determination of Validity of a Set of Observations.** Five charging observations (runs) obtained in accordance with this method shall be considered a valid set of observations for that day. No observation of an incomplete charge shall be included in a daily set of observations that is lower than the lowest reading for a complete charge. If both complete and incomplete charges have been observed, the daily set of observations shall include the five highest values observed. Four or three charging observations (runs) obtained in accordance with this method shall be considered a valid set of charging observations only where it is not possible to obtain five charging observations, because visual interferences (see Section 11.1.5) or inclement weather prevent a clear view of the charging system during charging. However, observations from three or four charges that satisfy these requirements shall not be considered a valid set of charging observations if use of such set of observations in a calculation under Section 12.4 would cause the value of A to be less than 145.

11.1.9 **Log Average.** For each day on which a valid daily set of observations is obtained, calculate the daily 30-day rolling log average of seconds of visible emissions from the charging operation for each battery using these data and the 29 previous valid daily sets of observations, in accordance with Section 12.4.

11.2 **Procedure for Determining VE from Coke Oven Door Areas.** The intent of this procedure is to determine VE from coke oven door areas by carefully observing the door area from a standard distance while walking at a normal pace.

11.2.1 **Number of Runs.** Refer to § 63.309(c)(1) of this part for the appropriate number of runs.

11.2.2 **Battery Traverse.** To conduct a battery traverse, walk the length of the battery on the outside of the pusher machine and quench car tracks at a steady, normal walking pace, pausing to make appropriate entries on the door area inspection sheet (Figure 303-2). A single test run consists of two timed traverses, one for the coke side and one for the push side. The walking pace shall be such that the duration of the traverse does not exceed an average of

4 seconds per oven door, excluding time spent moving around stationary obstructions or waiting for other obstructions to move from positions blocking the view of a series of doors. Extra time is allowed for each leak (a maximum of 10 additional seconds for each leaking door) for the observer to make the proper notation. A walking pace of 3 seconds per oven door has been found to be typical. Record the actual traverse time with a stopwatch.

11.2.2.1 Include in the traverse time only the time spent observing the doors and recording door leaks. To measure actual traverse time, use an accumulative-type stopwatch with unit divisions of 0.5 seconds or less. Exclude interruptions to the traverse and time required for the observer to move to positions where the view of the battery is unobstructed, or for obstructions, such as the door machine, to move from positions blocking the view of a series of doors.

11.2.2.2 Various situations may arise that will prevent the observer from viewing a door or a series of doors. Prior to the door inspection, the owner or operator may elect to temporarily suspend charging operations for the duration of the inspection, so that all of the doors can be viewed by the observer. The observer has two options for dealing with obstructions to view: (a) Stop the stopwatch and wait for the equipment to move or the fugitive emissions to dissipate before completing the traverse; or (b) stop the stopwatch, skip the affected ovens, and move to an unobstructed position to continue the traverse. Restart the stopwatch and continue the traverse. After the completion of the traverse, if the equipment has moved or the fugitive emissions have dissipated, inspect the affected doors. If the equipment is still preventing the observer from viewing the doors, then the affected doors may be counted as not observed. If option (b) is used because of doors blocked by machines during charging operations, then, of the affected doors, exclude the door from the most recently charged oven from the inspection. Record the oven numbers and make an appropriate notation under "Comments" on the door area inspection sheet (Figure 303-2).

11.2.2.3 When batteries have sheds to control emissions, conduct the inspection from outside the shed unless the doors cannot be adequately viewed. In this case, conduct the inspection from the bench. Be aware of special safety considerations pertinent to walking on the bench and follow the instructions of company personnel on the required equipment and procedures. If possible, conduct the bench traverse

whenever the bench is clear of the door machine and hot coke guide.

11.2.3 Observations. Record all the information requested at the top of the door area inspection sheet (Figure 303-2), including the number of non-operating ovens. Record the clock time at the start of the traverse on each side of the battery. Record which side is being inspected (*i.e.*, coke side or push side). Other information may be recorded at the discretion of the observer, such as the location of the leak (*e.g.*, top of the door, chuck door, etc.), the reason for any interruption of the traverse, or the position of the sun relative to the battery and sky conditions (*e.g.*, overcast, partly sunny, etc.).

11.2.3.1 Begin the test run by starting the stopwatch and traversing either the coke side or the push side of the battery. After completing one side, stop the watch. Complete this procedure on the other side. If inspecting more than one battery, the observer may view the push sides and the coke sides sequentially.

11.2.3.2 During the traverse, look around the entire perimeter of each oven door. The door is considered leaking if VE are detected in the coke oven door area. The coke oven door area includes the entire area on the vertical face of a coke oven between the bench and the top of the battery between two adjacent buck stays (*e.g.*, the oven door, chuck door, between the masonry brick, buck stay or jamb, or other sources). Record the oven number and make the appropriate notation on the door area inspection sheet (Figure 303-2).

Note: Multiple VE from the same door area (*e.g.*, VE from both the chuck door and the push side door) are counted as only one emitting door, not as multiple emitting doors.

11.2.3.3 Do not record the following sources as door area VE:

11.2.3.3.1 VE from ovens with doors removed. Record the oven number and make an appropriate notation under "Comments;"

11.2.3.3.2 VE from ovens taken out of service. The owner or operator shall notify the observer as to which ovens are out of service. Record the oven number and make an appropriate notation under "Comments;" or

11.2.3.3.3 VE from hot coke that has been spilled on the bench as a result of pushing.

11.2.4 Criteria for Acceptance. After completing the run, calculate the maximum time allowed to observe the ovens using the equation in Section 12.2. If the total traverse time exceeds T, void the run, and conduct another run to satisfy the requirements of § 63.309(c)(1) of this part.

11.2.5 Percent Leaking Doors. For each day on which a valid observation is obtained, calculate the daily 30-day rolling average for each battery using these data and the 29 previous valid daily observations, in accordance with Section 12.5.

11.3 Procedure for Determining VE from Topside Port Lids and Offtake Systems.

11.3.1 Number of Runs. Refer to § 63.309(c)(1) of this part for the number of runs to be conducted. Simultaneous runs or separate runs for the topside port lids and offtake systems may be conducted.

11.3.2 Battery Traverse. To conduct a topside traverse of the battery, walk the length of the battery at a steady, normal walking pace, pausing only to make appropriate entries on the topside inspection sheet (Figure 303-3). The walking pace shall not exceed an average rate of 4 seconds per oven, excluding time spent moving around stationary obstructions or waiting for other obstructions to move from positions blocking the view. Extra time is allowed for each leak for the observer to make the proper notation. A walking pace of 3 seconds per oven is typical. Record the actual traverse time with a stopwatch.

11.3.3 Topside Port Lid Observations. To observe lids of the ovens involved in the charging operation, the observer shall wait to view the lids until approximately 5 minutes after the completion of the charge. Record all the information requested on the topside inspection sheet (Figure 303-3). Record the clock time when traverses begin and end. If the observer's view is obstructed during the traverse (*e.g.*, steam from the coke wharf, larry car, etc.), follow the guidelines given in Section 11.2.2.2.

11.3.3.1 To perform a test run, conduct a single traverse on the topside of the battery. The observer shall walk near the center of the battery but may deviate from this path to avoid safety hazards (such as open or closed charging ports, luting buckets, lid removal bars, and topside port lids that have been removed) and any other obstacles. Upon noting VE from the topside port lid(s) of an oven, record the oven number and port number, then resume the traverse. If any oven is dampered-off from the collecting main for decarbonization, note this under "Comments" for that particular oven.

Note: Count the number of topside ports, not the number of points, exhibiting VE, *i.e.*, if a topside port has several points of VE, count this as one port exhibiting VE.

11.3.3.2 Do not count the following as topside port lid VE:

11.3.3.2.1 VE from between the brickwork and oven lid casing or VE from cracks in the oven brickwork. Note these VE under "Comments;"

11.3.3.2.2 VE from topside ports involved in a charging operation. Record the oven number, and make an appropriate notation (*e.g.*, not observed because ports open for charging) under "Comments;"

11.3.3.2.3 Topside ports having maintenance work done. Record the oven number and make an appropriate notation under "Comments;" or

11.3.3.2.4 Condensing water from wet-sealing material. Ports with only visible condensing water from wet-sealing material are counted as observed but not as having VE.

11.3.3.2.5 Visible emissions from the flue inspection ports and caps.

11.3.4 Offtake Systems

Observations. To perform a test run, traverse the battery as in Section

11.3.3.1. Look ahead and back two to four ovens to get a clear view of the entire offtake system for each oven. Consider visible emissions from the following points as offtake system VE: (a) the flange between the gooseneck and collecting main ("saddle"), (b) the junction point of the standpipe and oven ("standpipe base"), (c) the other parts of the offtake system (*e.g.*, the standpipe cap), and (d) the junction points with ovens and flanges of jumper pipes.

11.3.4.1 Do not stray from the traverse line in order to get a "closer look" at any part of the offtake system unless it is to distinguish leaks from interferences from other sources or to avoid obstacles.

11.3.4.2 If the centerline does not provide a clear view of the entire offtake system for each oven (*e.g.*, when standpipes are longer than 15 feet), the observer may conduct the traverse farther from (rather than closer to) the offtake systems.

11.3.4.3 Upon noting a leak from an offtake system during a traverse, record the oven number. Resume the traverse. If the oven is dampered-off from the collecting main for decarbonization and VE are observed, note this under "Comments" for that particular oven.

11.3.4.4 If any part or parts of an offtake system have VE, count it as one emitting offtake system. Each stationary jumper pipe is considered a single offtake system.

11.3.4.5 Do not count standpipe caps open for a decarbonization period or standpipes of an oven being charged as source of offtake system VE. Record the oven number and write "Not

observed" and the reason (*i.e.*, decarb or charging) under "Comments."

Note: VE from open standpipes of an oven being charged count as charging emissions. All VE from closed standpipe caps count as offtake leaks.

11.3.5 Criteria for Acceptance. After completing the run (allow 2 traverses for batteries with double mains), calculate the maximum time allowed to observe the topside port lids and/or offtake systems using the equation in Section 12.3. If the total traverse time exceeds T, void the run and conduct another run to satisfy the requirements of § 63.309(c)(1) of this part.

11.3.6 In determining the percent leaking topside port lids and percent leaking offtake systems, do not include topside port lids or offtake systems with VE from the following ovens:

11.3.6.1 Empty ovens, including ovens undergoing maintenance, which are properly dampered off from the main.

11.3.6.2 Ovens being charged or being pushed.

11.3.6.3 Up to 3 full ovens that have been dampered off from the main prior to pushing.

11.3.6.4 Up to 3 additional full ovens in the pushing sequence that have been dampered off from the main for offtake system cleaning, for decarbonization, for safety reasons, or when a charging/pushing schedule involves widely separated ovens (*e.g.*, a Marquard system); or that have been dampered off from the main for maintenance near the end of the coking cycle. Examples of reasons that ovens are dampered off for safety reasons are to avoid exposing workers in areas with insufficient clearance between standpipes and the larry car, or in areas where workers could be exposed to flames or hot gases from open standpipes, and to avoid the potential for removing a door on an oven that is not dampered off from the main.

11.3.7 Percent Leaking Topside Port Lids and Offtake Systems. For each day on which a valid observation is obtained, calculate the daily 30-day rolling average for each battery using these data and the 29 previous valid daily observations, in accordance with Sections 12.6 and 12.7.

11.4 Procedure for Determining VE from Collecting Mains.

11.4.1 Traverse. To perform a test run, traverse both the collecting main catwalk and the battery topside along the side closest to the collecting main. If the battery has a double main, conduct two sets of traverses for each run, *i.e.*, one set for each main.

11.4.2 Data Recording. Upon noting VE from any portion of a collection

main, identify the source and approximate location of the source of VE and record the time under "Collecting main" on Figure 303-3; then resume the traverse.

11.4.3 Collecting Main Pressure Check. After the completion of the door traverse, the topside port lids, and offtake systems, compare the collecting main pressure during the inspection to the collecting main pressure during the previous 8 to 24 hours. Record the following: (a) the pressure during inspection, (b) presence of pressure deviation from normal operations, and (c) the explanation for any pressure deviation from normal operations, if any, offered by the operators. The owner or operator of the coke battery shall maintain the pressure recording equipment and conduct the quality assurance/quality control (QA/QC) necessary to ensure reliable pressure readings and shall keep the QA/QC records for at least 6 months. The observer may periodically check the QA/QC records to determine their completeness. The owner or operator shall provide access to the records within 1 hour of an observer's request.

12.0 Data Analysis and Calculations

12.1 Nomenclature.

A = 150 or the number of valid observations (runs). The value of A shall not be less than 145, except for purposes of determinations under § 63.306(c) (work practice plan implementation) or § 63.306(d) (work practice plan revisions) of this part. No set of observations shall be considered valid for such a recalculation that otherwise would not be considered a valid set of observations for a calculation under this paragraph.

D_i = Number of doors on non-operating ovens.

D_{no} = Number of doors not observed.

D_{ob} = Total number of doors observed on operating ovens.

D_t = Total number of oven doors on the battery.

e = 2.72

J = Number of stationary jumper pipes.

L = Number of doors with VE.

L_{tb} = Yard-equivalent reading.

L_s = Number of doors with VE observed from the bench under sheds.

L_y = Number of doors with VE observed from the yard.

L_y = Number of doors with VE observed from the yard on the push side.

ln = Natural logarithm.

N = Total number of ovens in the battery.

N_i = Total number of inoperable ovens.

P_{NO} = Number of ports not observed.

P_{ovn} = Number of ports per oven.

P_{VE} = Number of topside port lids with VE.
 PLD = Percent leaking coke oven doors for the test run.
 PLL = Percent leaking topside port lids for the run.
 PLO = Percent leaking offtake systems.
 T = Total time allowed for traverse, seconds.

T_{ovn} = Number of offtake systems (excluding jumper pipes) per oven.
 T_{NO} = Number of offtake systems not observed.
 T_{VE} = Number of offtake systems with VE.
 X_i = Seconds of VE during the ith charge.

Z = Number of topside port lids or offtake systems with VE.

12.2 Criteria for Acceptance for VE Determinations from Coke Oven Door Areas. After completing the run, calculate the maximum time allowed to observe the ovens using the following equation:

$$T = (4 \times D_i) + (10 \times L) \quad \text{Eq. 303-1}$$

12.3 Criteria for Acceptance for VE Determinations from Topside Port Lids and Offtake Systems. After completing

the run (allow 2 traverses for batteries with double mains), calculate the maximum time allowed to observe the

topside port lids and/or offtake systems by the following equation:

$$T = (4 \times N) + (10 \times Z) \quad \text{Eq. 303-2}$$

12.4 Average Duration of VE from Charging Operations. Use Equation 303-3 to calculate the daily 30-day rolling log average of seconds of visible emissions from the charging operation for each battery using these current day's observations and the 29 previous valid daily sets of observations.

$$\text{logarithmic average} = e^y - 1 = \frac{\ln(X_1 + 1) + \ln(X_2 + 1) + \dots + \ln(X_A + 1)}{A} \quad \text{Eq. 303-3}$$

12.5 Percent Leaking Doors (PLD). Determine the total number of doors for which observations were made on the coke oven battery as follows:

$$D_{ob} = (2 \times N) - (D_i + D_{no}) \quad \text{Eq. 303-4}$$

12.5.1 For each test run (one run includes both the coke side and the push side traverses), sum the number of doors with door area VE. For batteries subject to an approved alternative standard under § 63.305 of this part, calculate the push side and the coke side PLD separately.

12.5.2 Calculate percent leaking doors by using Equation 303-5:

$$PLD = \frac{L_y}{D_{ob}} \times 100 \quad \text{Eq. 303-5}$$

12.5.3 When traverses are conducted from the bench under sheds, calculate the coke side and the push side separately. Use Equation 303-6 to calculate a yard-equivalent reading:

$$L_b = L_s - (N \times 0.06) \quad \text{Eq. 303-6}$$

If L_b is less than zero, use zero for L_b in Equation 303-7 in the calculation of PLD.

12.5.3.1 Use Equation 303-7 to calculate PLD:

$$PLD = \frac{L_b + L_y}{D_{ob}} \times 100 \quad \text{Eq. 303-7}$$

Round off PLD to the nearest hundredth of 1 percent and record as the percent leaking coke oven doors for the run.

12.5.3.2 Average Percent Leaking Doors. Use Equation 303-8 to calculate the daily 30-day rolling average percent leaking doors for each battery using these current day's observations and the 29 previous valid daily sets of observations.

$$PLD_{(30\text{-day})} = \frac{(PLD_1 + PLD_2 + \dots + PLD_{30})}{30} \quad \text{Eq. 303-8}$$

12.6 Topside Port Lids. Determine the percent leaking topside port lids for each run as follows:

$$PLL = \frac{P_{VE}}{P_{ovn}(N - N_i) - P_{NO}} \times 100 \quad \text{Eq. 303-9}$$

12.6.1 Round off this percentage to the nearest hundredth of 1 percent and record this percentage as the percent leaking topside port lids for the run.

12.6.2 Average Percent Leaking Topside Port Lids. Use Equation 303-10 to calculate the daily 30-day rolling average percent leaking topside port lids for each battery using these current day's observations and the 29 previous valid daily sets of observations.

$$\text{PLL (30-day)} = \frac{(\text{PLL}_1 + \text{PLL}_2 + \dots + \text{PLL}_{30})}{30} \quad \text{Eq. 303-10}$$

12.7 Offtake Systems. Determine the percent leaking offtake systems for the run as follows:

$$PLO = \frac{T_{VE}}{T_{Ovn}(N - N_i) + J - T_{NO}} \times 100 \quad \text{Eq. 303-11}$$

12.7.1 Round off this percentage to the nearest hundredth of 1 percent and record this percentage as the percent leaking offtake systems for the run.

12.7.2 Average Percent Leaking Offtake Systems. Use Equation 303–12 to calculate the daily 30-day rolling average percent leaking offtake systems for each battery using these current day's observations and the 29 previous valid daily sets of observations.

$$\text{PLO (30-day)} = \frac{(\text{PLO}_1 + \text{PLO}_2 \dots + \text{PLO}_{30})}{30} \quad \text{Eq. 303-12}$$

13.0 Method Performance. [Reserved]

14.0 Pollution Prevention. [Reserved]

15.0 Waste Management. [Reserved]

16.0 References.

1. Missan, R., and A. Stein. Guidelines for Evaluation of Visible Emissions Certification, Field Procedures, Legal Aspects, and Background Material. U.S. Environmental Protection Agency. EPA Publication No. EPA-340/1-75-007. April 1975.

2. Wohlschlegel, P., and D. E. Wagoner. Guideline for Development of a Quality Assurance Program: Volume IX—Visual Determination of Opacity Emission from Stationary Sources. U.S. Environmental Protection Agency. EPA Publication No. EPA-650/4-74-005i. November 1975.

3. U.S. Occupational Safety and Health Administration. Code of Federal Regulations. Title 29, Chapter XVII, Section 1910.1029(g). Washington, D.C. Government Printing Office. July 1, 1990.

4. U.S. Environmental Protection Agency. National Emission Standards for Hazardous Air Pollutants; Coke Oven Emissions from Wet-Coal Charged By-Product Coke Oven Batteries; Proposed Rule and Notice of Public Hearing. Washington, D.C. **Federal Register**. Vol. 52, No. 78 (13586). April 23, 1987.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

Company name:

Battery no.:

Date:

Run no.:

City, State:

Observer name:

Company representative(s):

[illegible]

Figure 303–1. Charging System Inspection

Company name:
Battery no.:
Date:
City, State:
Total no. of ovens in battery:
Observer name:
Certification expiration date:
Inoperable ovens:
Company representative(s):
Traverse time CS:
Traverse time PS:
Valid run (Y or N):

Figure 303–2. Door Area Inspection.

[illegible]

Method 303A—Determination of Visible Emissions From Nonrecovery Coke Oven Batteries

Note: This method does not include all of the specifications pertaining to observer certification. Some material is incorporated by reference from other methods in this part and in appendix A to 40 CFR Part 60. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of Method 9 and Method 303.

1.1 Applicability. This method is applicable for the determination of visible emissions (VE) from leaking doors at nonrecovery coke oven batteries.

2.1 A certified observer visually determines the VE from coke oven battery sources while walking at a

normal pace. This method does not require that opacity of emissions be determined or that magnitude be differentiated.

3.1 *Bench* means the platform structure in front of the oven doors.

3.2 *Coke oven door* means each end enclosure on the push side and the coking side of an oven.

3.3 *Coke side* means the side of a battery from which the coke is discharged from ovens at the end of the coking cycle.

3.4 *Nonrecovery coke oven battery* means a source consisting of a group of ovens connected by common walls and operated as a unit, where coal undergoes destructive distillation under negative pressure to produce coke, and which is designed for the combustion of coke oven gas from which by-products are not recovered.

3.5 *Operating oven* means any oven not out of operation for rebuild or maintenance work extensive enough to require the oven to be skipped in the charging sequence.

3.6 *Oven* means a chamber in the coke oven battery in which coal undergoes destructive distillation to produce coke.

3.7 *Push side* means the side of the battery from which the coke is pushed from ovens at the end of the coking cycle.

3.8 *Run* means the observation of visible emissions from coke oven doors in accordance with this method.

3.9 *Shed* means an enclosure that covers the side of the coke oven battery, captures emissions from pushing operations and from leaking coke oven doors on the coke side or push side of the coke oven battery, and routes the emissions to a control device or system.

3.10 *Traverse time* means accumulated time for a traverse as measured by a stopwatch. Traverse time includes time to stop and write down oven numbers but excludes time waiting for obstructions of view to clear or for time to walk around obstacles.

3.11 *Visible Emissions or VE* means any emission seen by the unaided (except for corrective lenses) eye, excluding steam or condensing water.

4.0 *Interferences.* [Reserved]

5.0 *Safety*

5.1 *Disclaimer.* This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

5.2 *Safety Training.* Because coke oven batteries have hazardous environments, the training materials and the field training (Section 10.0) shall cover the precautions required by

the company to address health and safety hazards. Special emphasis shall be given to the Occupational Safety and Health Administration (OSHA) regulations pertaining to exposure of coke oven workers (see Reference 3 in Section 16.0). In general, the regulation requires that special fire-retardant clothing and respirators be worn in certain restricted areas of the coke oven battery. The OSHA regulation also prohibits certain activities, such as chewing gum, smoking, and eating in these areas.

6.0 *Equipment and Supplies.* [Reserved]

7.0 *Reagents and Standards* [Reserved]

8.0 *Sample Collection, Preservation, Transport, and Storage.* [Reserved]

9.0 *Quality Control.* [Reserved]

10.0 *Calibration and Standardization.*

10.1 *Training.* This method requires only the determination of whether VE occur and does not require the determination of opacity levels; therefore, observer certification according to Method 9 in Appendix A to Part 60 is not required. However, the first-time observer (trainee) shall have attended the lecture portion of the Method 9 certification course. Furthermore, before conducting any VE observations, an observer shall become familiar with nonrecovery coke oven battery operations and with this test method by observing for a minimum of 4 hours the operation of a nonrecovery coke oven battery in the presence of personnel experienced in performing Method 303 assessments.

11.0 *Procedure*

The intent of this procedure is to determine VE from coke oven door areas by carefully observing the door area while walking at a normal pace.

11.1 *Number of Runs.* Refer to § 63.309(c)(1) of this part for the appropriate number of runs.

11.2 *Battery Traverse.* To conduct a battery traverse, walk the length of the battery on the outside of the pusher machine and quench car tracks at a steady, normal walking pace, pausing to make appropriate entries on the door area inspection sheet (Figure 303A-1). The walking pace shall be such that the duration of the traverse does not exceed an average of 4 seconds per oven door, excluding time spent moving around stationary obstructions or waiting for other obstructions to move from positions blocking the view of a series of doors. Extra time is allowed for each leak (a maximum of 10 additional seconds for each leaking door) for the

observer to make the proper notation. A walking pace of 3 seconds per oven door has been found to be typical. Record the actual traverse time with a stopwatch. A single test run consists of two timed traverses, one for the coke side and one for the push side.

11.2.1 Various situations may arise that will prevent the observer from viewing a door or a series of doors. The observer has two options for dealing with obstructions to view: (a) Wait for the equipment to move or the fugitive emissions to dissipate before completing the traverse; or (b) skip the affected ovens and move to an unobstructed position to continue the traverse. Continue the traverse. After the completion of the traverse, if the equipment has moved or the fugitive emissions have dissipated, complete the traverse by inspecting the affected doors. Record the oven numbers and make an appropriate notation under "Comments" on the door area inspection sheet (Figure 303A-1).

Note: Extra time incurred for handling obstructions is not counted in the traverse time.

11.2.2 When batteries have sheds to control pushing emissions, conduct the inspection from outside the shed, if the shed allows such observations, or from the bench. Be aware of special safety considerations pertinent to walking on the bench and follow the instructions of company personnel on the required equipment and operations procedures. If possible, conduct the bench traverse whenever the bench is clear of the door machine and hot coke guide.

11.3 *Observations.* Record all the information requested at the top of the door area inspection sheet (Figure 303A-1), including the number of non-operating ovens. Record which side is being inspected, *i.e.*, coke side or push side. Other information may be recorded at the discretion of the observer, such as the location of the leak (*e.g.*, top of the door), the reason for any interruption of the traverse, or the position of the sun relative to the battery and sky conditions (*e.g.*, overcast, partly sunny, etc.).

11.3.1 Begin the test run by traversing either the coke side or the push side of the battery. After completing one side, traverse the other side.

11.3.2 During the traverse, look around the entire perimeter of each oven door. The door is considered leaking if VE are detected in the coke oven door area. The coke oven door area includes the entire area on the vertical face of a coke oven between the bench and the top of the battery and the

17.0 Tables, Diagrams, Flowcharts, and Validation Data

[illegible]

Figure 303A-1. Door Area Inspection

Method 304A: Determination of Biodegradation Rates of Organic Compounds (Vent Option)**1.0 Scope and Application**

1.1 Applicability. This method is applicable for the determination of biodegradation rates of organic compounds in an activated sludge process. The test method is designed to evaluate the ability of an aerobic biological reaction system to degrade or destroy specific components in waste streams. The method may also be used to determine the effects of changes in wastewater composition on operation. The biodegradation rates determined by utilizing this method are not representative of a full-scale system. The rates measured by this method shall be used in conjunction with the procedures listed in appendix C of this part to calculate the fraction emitted to the air versus the fraction biodegraded.

2.0 Summary of Method

2.1 A self-contained benchtop bioreactor system is assembled in the laboratory. A sample of mixed liquor is added and the waste stream is then fed continuously. The benchtop bioreactor is operated under conditions nearly identical to the target full-scale activated sludge process. Bioreactor temperature, dissolved oxygen concentration, average residence time in the reactor, waste composition, biomass concentration, and biomass composition of the full-scale process are the parameters which are duplicated in the benchtop bioreactor. Biomass shall be removed from the target full-scale activated sludge unit and held for no more than 4 hours prior to use in the benchtop bioreactor. If antifoaming agents are used in the full-scale system, they shall also be used in the benchtop bioreactor. The feed flowing into and the effluent exiting the benchtop bioreactor are analyzed to determine the biodegradation rates of the target compounds. The flow rate of the exit vent is used to calculate the concentration of target compounds (utilizing Henry's law) in the exit gas stream. If Henry's law constants for the compounds of interest are not known, this method cannot be used in the determination of the biodegradation rate and Method 304B is the suggested method. The choice of analytical methodology for measuring the compounds of interest at the inlet and outlet to the benchtop bioreactor are left to the discretion of the source, except where validated methods are available.

3.0 Definitions. [Reserved]**4.0 Interferences. [Reserved]****5.0 Safety**

5.1 If explosive gases are produced as a byproduct of biodegradation and could realistically pose a hazard, closely monitor headspace concentration of these gases to ensure laboratory safety. Placement of the benchtop bioreactor system inside a laboratory hood is recommended regardless of byproducts produced.

6.0 Equipment and Supplies

Note: Figure 304A-1 illustrates a typical laboratory apparatus used to measure biodegradation rates. While the following description refers to Figure 304A-1, the EPA recognizes that alternative reactor configurations, such as alternative reactor shapes and locations of probes and the feed inlet, will also meet the intent of this method. Ensure that the benchtop bioreactor system is self-contained and isolated from the atmosphere (except for the exit vent stream) by leak-checking fittings, tubing, etc.

6.1 Benchtop Bioreactor. The biological reaction is conducted in a biological oxidation reactor of at least 6 liters capacity. The benchtop bioreactor is sealed and equipped with internal probes for controlling and monitoring dissolved oxygen and internal temperature. The top of the reactor is equipped for aerators, gas flow ports, and instrumentation (while ensuring that no leaks to the atmosphere exist around the fittings).

6.2 Aeration gas. Aeration gas is added to the benchtop bioreactor through three diffusers, which are glass tubes that extend to the bottom fifth of the reactor depth. A pure oxygen pressurized cylinder is recommended in order to maintain the specified oxygen concentration. Install a blower (e.g., Diaphragm Type, 15 SCFH capacity) to blow the aeration gas into the reactor diffusers. Measure the aeration gas flow rate with a rotameter (e.g., 0-15 SCFH recommended). The aeration gas will rise through the benchtop bioreactor, dissolving oxygen into the mixture in the process. The aeration gas must provide sufficient agitation to keep the solids in suspension. Provide an exit for the aeration gas from the top flange of the benchtop bioreactor through a water-cooled (e.g., Allihn-type) vertical condenser. Install the condenser through a gas-tight fitting in the benchtop bioreactor closure. Install a splitter which directs a portion of the gas to an exit vent and the rest of the gas through an air recycle pump back to the benchtop bioreactor. Monitor and record the flow rate through the exit

vent at least 3 times per day throughout the day.

6.3 Wastewater Feed. Supply the wastewater feed to the benchtop bioreactor in a collapsible low-density polyethylene container or collapsible liner in a container (e.g., 20 L) equipped with a spigot cap (collapsible containers or liners of other material may be required due to the permeability of some volatile compounds through polyethylene). Obtain the wastewater feed by sampling the wastewater feed in the target process. A representative sample of wastewater shall be obtained from the piping leading to the aeration tank. This sample may be obtained from existing sampling valves at the discharge of the wastewater feed pump, or collected from a pipe discharging to the aeration tank, or by pumping from a well-mixed equalization tank upstream from the aeration tank. Alternatively, wastewater can be pumped continuously to the laboratory apparatus from a bleed stream taken from the equalization tank of the full-scale treatment system.

6.3.1 Refrigeration System. Keep the wastewater feed cool by ice or by refrigeration to 4°C. If using a bleed stream from the equalization tank, refrigeration is not required if the residence time in the bleed stream is less than five minutes.

6.3.2 Wastewater Feed Pump. The wastewater is pumped from the refrigerated container using a variable-speed peristaltic pump drive equipped with a peristaltic pump head. Add the feed solution to the benchtop bioreactor through a fitting on the top flange. Determine the rate of feed addition to provide a retention time in the benchtop bioreactor that is numerically equivalent to the retention time in the full-scale system. The wastewater shall be fed at a rate sufficient to achieve 90 to 100 percent of the full-scale system residence time.

6.3.3 Treated wastewater feed. The benchtop bioreactor effluent exits at the bottom of the reactor through a tube and proceeds to the clarifier.

6.4 Clarifier. The effluent flows to a separate closed clarifier that allows separation of biomass and effluent (e.g., 2-liter pear-shaped glass separatory funnel, modified by removing the stopcock and adding a 25-mm OD glass tube at the bottom). Benchtop bioreactor effluent enters the clarifier through a tube inserted to a depth of 0.08 m (3 in.) through a stopper at the top of the

clarifier. System effluent flows from a tube inserted through the stopper at the top of the clarifier to a drain (or sample bottle when sampling). The underflow from the clarifier leaves from the glass tube at the bottom of the clarifier. Flexible tubing connects this fitting to the sludge recycle pump. This pump is coupled to a variable speed pump drive. The discharge from this pump is returned through a tube inserted in a port on the side of the benchtop bioreactor. An additional port is provided near the bottom of the benchtop bioreactor for sampling the reactor contents. The mixed liquor from the benchtop bioreactor flows into the center of the clarifier. The clarified system effluent separates from the biomass and flows through an exit near the top of the clarifier. There shall be no headspace in the clarifier.

6.5 Temperature Control Apparatus. Capable of maintaining the system at a temperature equal to the temperature of the full-scale system. The average temperature should be maintained within ± 2 °C of the set point.

6.5.1 Temperature Monitoring Device. A resistance type temperature probe or a thermocouple connected to a temperature readout with a resolution of 0.1 °C or better.

6.5.2 Benchtop Bioreactor Heater. The heater is connected to the temperature control device.

6.6 Oxygen Control System. Maintain the dissolved oxygen concentration at the levels present in the full-scale system. Target full-scale activated sludge systems with dissolved oxygen concentration below 2 mg/L are required to maintain the dissolved oxygen concentration in the benchtop bioreactor within 0.5 mg/L of the target dissolved oxygen level. Target full-scale activated sludge systems with dissolved oxygen concentration above 2 mg/L are required to maintain the dissolved oxygen concentration in the benchtop bioreactor within 1.5 mg/L of the target dissolved oxygen concentration; however, for target full-scale activated sludge systems with dissolved oxygen concentrations above 2 mg/L, the dissolved oxygen concentration in the benchtop bioreactor may not drop below 1.5 mg/L. If the benchtop bioreactor is

outside the control range, the dissolved oxygen is noted and the reactor operation is adjusted.

6.6.1 Dissolved Oxygen Monitor. Dissolved oxygen is monitored with a polarographic probe (gas permeable membrane) connected to a dissolved oxygen meter (*e.g.*, 0 to 15 mg/L, 0 to 50 °C).

6.6.2 Benchtop Bioreactor Pressure Monitor. The benchtop bioreactor pressure is monitored through a port in the top flange of the reactor. This is connected to a gauge control with a span of 13-cm water vacuum to 13-cm water pressure or better. A relay is activated when the vacuum exceeds an adjustable setpoint which opens a solenoid valve (normally closed), admitting oxygen to the system. The vacuum setpoint controlling oxygen addition to the system shall be set at approximately 2.5 ± 0.5 cm water and maintained at this setting except during brief periods when the dissolved oxygen concentration is adjusted.

6.7 Connecting Tubing. All connecting tubing shall be Teflon or equivalent in impermeability. The only exception to this specification is the tubing directly inside the pump head of the wastewater feed pump, which may be Viton, Silicone or another type of flexible tubing.

Note: Mention of trade names or products does not constitute endorsement by the U.S. Environmental Protection Agency.

7.0 Reagents and Standards

7.1 Wastewater. Obtain a representative sample of wastewater at the inlet to the full-scale treatment plant if there is an existing full-scale treatment plant (see section 6.3). If there is no existing full-scale treatment plant, obtain the wastewater sample as close to the point of determination as possible. Collect the sample by pumping the wastewater into the 20-L collapsible container. The loss of volatiles shall be minimized from the wastewater by collapsing the container before filling, by minimizing the time of filling, and by avoiding a headspace in the container after filling. If the wastewater requires the addition of nutrients to support the biomass growth and maintain biomass characteristics, those nutrients are

added and mixed with the container contents after the container is filled.

7.2 Biomass. Obtain the biomass or activated sludge used for rate constant determination in the bench-scale process from the existing full-scale process or from a representative biomass culture (*e.g.*, biomass that has been developed for a future full-scale process). This biomass is preferentially obtained from a thickened acclimated mixed liquor sample. Collect the sample either by bailing from the mixed liquor in the aeration tank with a weighted container, or by collecting aeration tank effluent at the effluent overflow weir. Transport the sample to the laboratory within no more than 4 hours of collection. Maintain the biomass concentration in the benchtop bioreactor at the level of the full-scale system +10 percent throughout the sampling period of the test method.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Benchtop Bioreactor Operation. Charge the mixed liquor to the benchtop bioreactor, minimizing headspace over the liquid surface to minimize entrainment of mixed liquor in the circulating gas. Fasten the benchtop bioreactor headplate to the reactor over the liquid surface. Maintain the temperature of the contents of the benchtop bioreactor system at the temperature of the target full-scale system, ± 2 °C, throughout the testing period. Monitor and record the temperature of the benchtop bioreactor contents at least to the nearest 0.1 °C.

8.1.1 Wastewater Storage. Collect the wastewater sample in the 20-L collapsible container. Store the container at 4 °C throughout the testing period. Connect the container to the benchtop bioreactor feed pump.

8.1.2 Wastewater Flow Rate.

8.1.2.1 The hydraulic residence time of the aeration tank is calculated as the ratio of the volume of the tank (L) to the flow rate (L/min). At the beginning of a test, the container shall be connected to the feed pump and solution shall be pumped to the benchtop bioreactor at the required flow rate to achieve the calculated hydraulic residence time of wastewater in the aeration tank.

8.1.2.2 The target flow rate in the test apparatus is the same as the flow rate in the target full-scale process

$$Q_{\text{test}} = Q_{\text{fs}} \frac{L}{V_{\text{fs}}} \quad \text{Eq. 304A-1}$$

Where:

Q_{test} = wastewater flow rate (L/min)

Q_{fs} = average flow rate of full-scale process (L/min)

V_{fs} = volume of full-scale aeration tank (L)

multiplied by the ratio of benchtop bioreactor volume (e.g., 6 L) to the volume of the full-scale aeration tank. The hydraulic residence time shall be maintained at 90 to 100 percent of the residence time maintained in the full-scale unit. A nominal flow rate is set on the pump based on a pump calibration. Changes in the elasticity of the tubing in the pump head and the accumulation of material in the tubing affect this calibration. The nominal pumping rate shall be changed as necessary based on volumetric flow measurements. Discharge the benchtop bioreactor effluent to a wastewater storage, treatment, or disposal facility, except during sampling or flow measurement periods.

8.1.3 Sludge Recycle Rate. Set the sludge recycle rate at a rate sufficient to prevent accumulation in the bottom of the clarifier. Set the air circulation rate sufficient to maintain the biomass in suspension.

8.1.4 Benchtop Bioreactor Operation and Maintenance. Temperature, dissolved oxygen concentration, exit vent flow rate, benchtop bioreactor effluent flow rate, and air circulation rate shall be measured and recorded three times throughout each day of benchtop bioreactor operation. If other parameters (such as pH) are measured and maintained in the target full-scale unit, these parameters, where appropriate, shall be monitored and maintained to target full-scale specifications in the benchtop bioreactor. At the beginning of each sampling period (Section 8.2), sample the benchtop bioreactor contents for suspended solids analysis. Take this sample by loosening a clamp on a length of tubing attached to the lower side port. Determine the suspended solids gravimetrically by the Gooch crucible/glass fiber filter method for total suspended solids, in accordance with Standard Methods³ or equivalent. When necessary, sludge shall be wasted from the lower side port of the benchtop bioreactor, and the volume that is wasted shall be replaced with an equal volume of the reactor effluent. Add thickened activated sludge mixed liquor as necessary to the benchtop bioreactor

to increase the suspended solids concentration to the desired level. Pump this mixed liquor to the benchtop bioreactor through the upper side port (Item 24 in Figure 304A-1). Change the membrane on the dissolved oxygen probe before starting the test. Calibrate the oxygen probe immediately before the start of the test and each time the membrane is changed.

8.1.5 Inspection and Correction Procedures. If the feed line tubing becomes clogged, replace with new tubing. If the feed flow rate is not within 5 percent of target flow any time the flow rate is measured, reset pump or check the flow measuring device and measure flow rate again until target flow rate is achieved.

8.2 Test Sampling. At least two and one half hydraulic residence times after the system has reached the targeted specifications shall be permitted to elapse before the first sample is taken. Effluent samples of the clarifier discharge (Item 20 in Figure 304A-1) and the influent wastewater feed are collected in 40-mL septum vials to which two drops of 1:10 hydrochloric acid (HCl) in water have been added. Sample the clarifier discharge directly from the drain line. These samples will be composed of the entire flow from the system for a period of several minutes. Feed samples shall be taken from the feed pump suction line after temporarily stopping the benchtop bioreactor feed, removing a connector, and squeezing the collapsible feed container. Store both influent and effluent samples at 4 °C immediately after collection and analyze within 8 hours of collection.

8.2.1 Frequency of Sampling. During the test, sample and analyze the wastewater feed and the clarifier effluent at least six times. The sampling intervals shall be separated by at least 8 hours. During any individual sampling interval, sample the wastewater feed simultaneously with or immediately after the effluent sample. Calculate the relative standard deviation (RSD) of the amount removed (*i.e.*, effluent concentration—wastewater feed concentration). The RSD values shall be < 15 percent. If an RSD value is > 15 percent, continue sampling and

analyzing influent and effluent sets of samples until the RSD values are within specifications.

8.2.2 Sampling After Exposure of System to Atmosphere. If, after starting sampling procedures, the benchtop bioreactor system is exposed to the atmosphere (due to leaks, maintenance, etc.), allow at least one hydraulic residence time to elapse before resuming sampling.

9.0 Quality Control

9.1 Dissolved Oxygen. Fluctuation in dissolved oxygen concentration may occur for numerous reasons, including undetected gas leaks, increases and decreases in mixed liquor suspended solids resulting from cell growth and solids loss in the effluent stream, changes in diffuser performance, cycling of effluent flow rate, and overcorrection due to faulty or sluggish dissolved oxygen probe response. Control the dissolved oxygen concentration in the benchtop bioreactor by changing the proportion of oxygen in the circulating aeration gas. Should the dissolved oxygen concentration drift below the designated experimental condition, bleed a small amount of aeration gas from the system on the pressure side (*i.e.*, immediately upstream of one of the diffusers). This will create a vacuum in the system, triggering the pressure sensitive relay to open the solenoid valve and admit oxygen to the system. Should the dissolved oxygen concentration drift above the designated experimental condition, slow or stop the oxygen input to the system until the dissolved oxygen concentration approaches the correct level.

9.2 Sludge Wasting.

9.2.1 Determine the suspended solids concentration (section 8.1.4) at the beginning of a test, and once per day thereafter during the test. If the test is completed within a two day period, determine the suspended solids concentration after the final sample set is taken. If the suspended solids concentration exceeds the specified concentration, remove a fraction of the sludge from the benchtop bioreactor. The required volume of mixed liquor to remove is determined as follows:

$$V_w = V_r \left(\frac{S_m - S_s}{S_m} \right) \quad \text{Eq. 304A-2}$$

Where:

V_w is the wasted volume (Liters),

V_r is the volume of the benchtop bioreactor (Liters),

S_m is the measured solids (g/L), and
 S_s is the specified solids (g/L).

9.2.2 Remove the mixed liquor from the benchtop bioreactor by loosening a

clamp on the mixed liquor sampling tube and allowing the required volume to drain to a graduated flask. Clamp the tube when the correct volume has been

wasted. Replace the volume of the liquid wasted by pouring the same volume of effluent back into the

benchtop bioreactor. Dispose of the waste sludge properly.

9.3 Sludge Makeup. In the event that the suspended solids concentration is

lower than the specifications, add makeup sludge back into the benchtop bioreactor. Determine the amount of sludge added by the following equation:

$$V_w = V_r \left(\frac{S_s - S_m}{S_w} \right) \quad \text{Eq. 304A-3}$$

Where:

V_w is the volume of sludge to add (Liters),

V_r is the volume of the benchtop bioreactor (Liters),

S_w is the solids in the makeup sludge (g/L),

S_m is the measured solids (g/L), and S_s is the specified solids (g/L).

10.0 Calibration and Standardization

10.1 Wastewater Pump Calibration. Determine the wastewater flow rate by collecting the system effluent for a time period of at least one hour, and measuring the volume with a graduated cylinder. Record the collection time period and volume collected. Determine flow rate. Adjust the pump speed to deliver the specified flow rate.

10.2 Calibration Standards. Prepare calibration standards from pure certified standards in an aqueous medium. Prepare and analyze three concentrations of calibration standards for each target component (or for a mixture of components) in triplicate daily throughout the analyses of the test samples. At each concentration level, a single calibration shall be within 5 percent of the average of the three calibration results. The low and medium calibration standards shall bracket the expected concentration of the effluent (treated) wastewater. The medium and high standards shall bracket the expected influent concentration.

11.0 Analytical Procedures

11.1 Analysis. If the identity of the compounds of interest in the wastewater is not known, a representative sample of the wastewater shall be analyzed in order to identify all of the compounds of interest present. A gas chromatography/mass spectrometry screening method is recommended.

11.1.1 After identifying the compounds of interest in the wastewater, develop and/or use one or more analytical techniques capable of measuring each of those compounds (more than one analytical technique may be required, depending on the characteristics of the wastewater). Test Method 18, found in appendix A of 40 CFR 60, may be used as a guideline in developing the analytical technique. Purge and trap techniques may be used for analysis providing the target components are sufficiently volatile to make this technique appropriate. The limit of quantitation for each compound shall be determined (see reference 1). If the effluent concentration of any target compound is below the limit of quantitation determined for that compound, the operation of the Method 304 unit may be altered to attempt to increase the effluent concentration above the limit of quantitation. Modifications to the method shall be approved prior to the test. The request should be addressed to Method 304 contact, Emissions Measurement Center, Mail Drop 19, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711.

12.0 Data Analysis and Calculations

12.1 Nomenclature. The following symbols are used in the calculations.

C_i = Average inlet feed concentration for a compound of interest, as analyzed (mg/L)

C_o = Average outlet (effluent) concentration for a compound of interest, as analyzed (mg/L)

X = Biomass concentration, mixed liquor suspended solids (g/L)

t = Hydraulic residence time in the benchtop bioreactor (hours)

V = Volume of the benchtop bioreactor (L)

Q = Flow rate of wastewater into the benchtop bioreactor, average (L/hour)

12.2 Residence Time. The hydraulic residence time of the benchtop bioreactor is equal to the ratio of the volume of the benchtop bioreactor (L) to the flow rate (L/h):

$$t = \frac{V}{Q} \quad \text{Eq. 304A-4}$$

12.3 Rate of Biodegradation. Calculate the rate of biodegradation for each component with the following equation:

$$\text{Rate} \left(\frac{\text{mg}}{\text{L} \cdot \text{h}} \right) = \frac{C_i - C_o}{t} \quad \text{Eq. 304A-5}$$

12.4 First-Order Biorate Constant. Calculate the first-order biorate constant (K_1) for each component with the following equation:

$$K_1 \left(\frac{\text{L}}{\text{g} \cdot \text{h}} \right) = \frac{C_i - C_o}{t C_o X} \quad \text{Eq. 304A-6}$$

12.5 Relative Standard Deviation (RSD). Determine the standard deviation of both the influent and effluent sample

concentrations (S) using the following equation:

$$\text{RSD} = \frac{100}{\bar{S}} \left(\frac{\sum_{i=1}^n (S_i - \bar{S})^2}{(n-1)} \right)^{1/2} \quad \text{Eq. 304A-7}$$

12.6 Determination of Percent Air Emissions and Percent Biodegraded. Use the results from this test method and follow the applicable procedures in appendix C of 40 CFR part 63, entitled, "Determination of the Fraction Biodegraded (F_{bio}) in a Biological Treatment Unit" to determine F_{bio} .

13.0 *Method Performance, [Reserved]*

14.0 *Pollution Prevention, [Reserved]*

15.0 *Waste Management, [Reserved]*

16.0 *References*

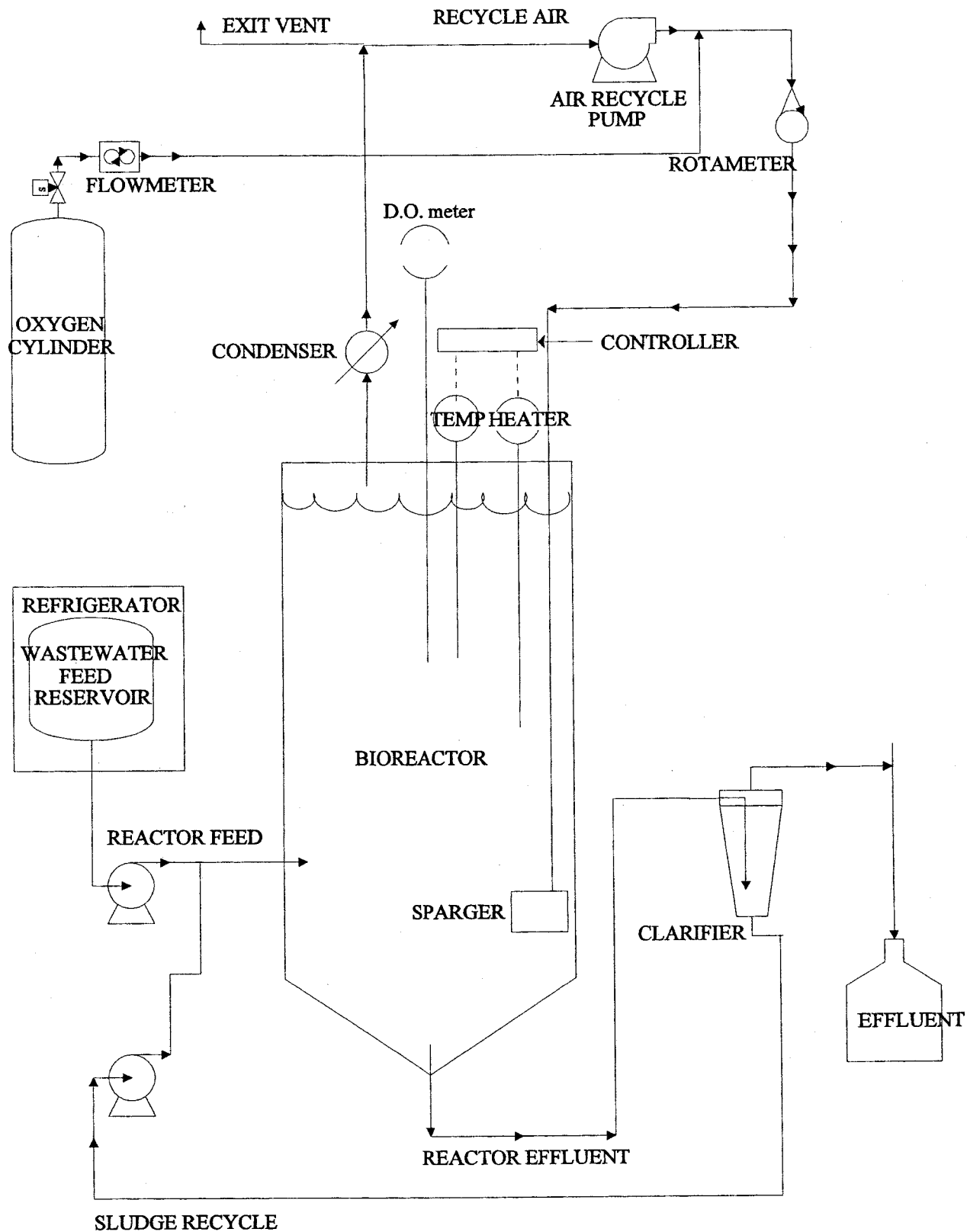
1. "Guidelines for data acquisition and data quality evaluation in Environmental Chemistry," Daniel MacDoughal, Analytical Chemistry, Volume 52, p. 2242, 1980.
2. Test Method 18, 40 CFR 60, appendix A.
3. Standard Methods for the Examination of Water and Wastewater, 16th Edition,

Method 209C, Total Suspended Solids Dried at 103–105 °C, APHA, 1985.

4. Water7, Hazardous Waste Treatment, Storage, and Disposal Facilities (TSDF)—Air Emission Models, U.S. Environmental Protection Agency, EPA-450/3-87-026, Review Draft, November 1989.

5. Chemdat7, Hazardous Waste Treatment, Storage, and Disposal Facilities (TSDF)—Air Emission Models, U.S. Environmental Protection Agency, EPA-450/3-87-026, Review Draft, November 1989.

17.0 Tables, Diagrams, Flowcharts, and Validation Data



EPA METHOD 304A VENT BIOREACTOR SYSTEM

Method 304B: Determination of Biodegradation Rates of Organic Compounds (Scrubber Option)

1.0 Scope and Application

1.1 Applicability. This method is applicable for the determination of biodegradation rates of organic compounds in an activated sludge process. The test method is designed to evaluate the ability of an aerobic biological reaction system to degrade or destroy specific components in waste streams. The method may also be used to determine the effects of changes in wastewater composition on operation. The biodegradation rates determined by utilizing this method are not representative of a full-scale system. Full-scale systems embody biodegradation and air emissions in competing reactions. This method measures biodegradation in absence of air emissions. The rates measured by this method shall be used in conjunction with the procedures listed in appendix C of this part to calculate the fraction emitted to the air versus the fraction biodegraded.

2.0 Summary of Method

2.1 A self-contained benchtop bioreactor system is assembled in the laboratory. A sample of mixed liquor is added and the waste stream is then fed continuously. The benchtop bioreactor is operated under conditions nearly identical to the target full-scale activated sludge process, except that air emissions are not a factor. The benchtop bioreactor temperature, dissolved oxygen concentration, average residence time in the reactor, waste composition, biomass concentration, and biomass composition of the target full-scale process are the parameters which are duplicated in the laboratory system. Biomass shall be removed from the target full-scale activated sludge unit and held for no more than 4 hours prior to use in the benchtop bioreactor. If antifoaming agents are used in the full-scale system, they shall also be used in the benchtop bioreactor. The feed flowing into and the effluent exiting the benchtop bioreactor are analyzed to determine the biodegradation rates of the target compounds. The choice of analytical methodology for measuring the compounds of interest at the inlet and outlet to the benchtop bioreactor are left to the discretion of the source, except where validated methods are available.

3.0 Definitions. [Reserved]

4.0 Interferences. [Reserved]

5.0 Safety

5.1 If explosive gases are produced as a byproduct of biodegradation and could realistically pose a hazard, closely monitor headspace concentration of these gases to ensure laboratory safety. Placement of the benchtop bioreactor system inside a laboratory hood is recommended regardless of byproducts produced.

6.0 Equipment and Supplies

Note: Figure 304B-1 illustrates a typical laboratory apparatus used to measure biodegradation rates. While the following description refers to Figure 304B-1, the EPA recognizes that alternative reactor configurations, such as alternative reactor shapes and locations of probes and the feed inlet, will also meet the intent of this method. Ensure that the benchtop bioreactor system is self-contained and isolated from the atmosphere by leak-checking fittings, tubing, etc.

6.1 Benchtop Bioreactor. The biological reaction is conducted in a biological oxidation reactor of at least 6-liters capacity. The benchtop bioreactor is sealed and equipped with internal probes for controlling and monitoring dissolved oxygen and internal temperature. The top of the benchtop bioreactor is equipped for aerators, gas flow ports, and instrumentation (while ensuring that no leaks to the atmosphere exist around the fittings).

6.2 Aeration gas. Aeration gas is added to the benchtop bioreactor through three diffusers, which are glass tubes that extend to the bottom fifth of the reactor depth. A pure oxygen pressurized cylinder is recommended in order to maintain the specified oxygen concentration. Install a blower (e.g., Diaphragm Type, 15 SCFH capacity) to blow the aeration gas into the benchtop bioreactor diffusers. Measure the aeration gas flow rate with a rotameter (e.g., 0-15 SCFH recommended). The aeration gas will rise through the benchtop bioreactor, dissolving oxygen into the mixture in the process. The aeration gas must provide sufficient agitation to keep the solids in suspension. Provide an exit for the aeration gas from the top flange of the benchtop bioreactor through a water-cooled (e.g., Allihn-type) vertical condenser. Install the condenser through a gas-tight fitting in the benchtop bioreactor closure. Design the system so that at least 10 percent of the gas flows through an alkaline scrubber containing 175 mL of 45 percent by weight solution of potassium hydroxide (KOH) and 5 drops of 0.2 percent

alizarin yellow dye. Route the balance of the gas through an adjustable scrubber bypass. Route all of the gas through a 1-L knock-out flask to remove entrained moisture and then to the intake of the blower. The blower recirculates the gas to the benchtop bioreactor.

6.3 Wastewater Feed. Supply the wastewater feed to the benchtop bioreactor in a collapsible low-density polyethylene container or collapsible liner in a container (e.g., 20 L) equipped with a spigot cap (collapsible containers or liners of other material may be required due to the permeability of some volatile compounds through polyethylene). Obtain the wastewater feed by sampling the wastewater feed in the target process. A representative sample of wastewater shall be obtained from the piping leading to the aeration tank. This sample may be obtained from existing sampling valves at the discharge of the wastewater feed pump, or collected from a pipe discharging to the aeration tank, or by pumping from a well-mixed equalization tank upstream from the aeration tank. Alternatively, wastewater can be pumped continuously to the laboratory apparatus from a bleed stream taken from the equalization tank of the full-scale treatment system.

6.3.1 Refrigeration System. Keep the wastewater feed cool by ice or by refrigeration to 4°C. If using a bleed stream from the equalization tank, refrigeration is not required if the residence time in the bleed stream is less than five minutes.

6.3.2 Wastewater Feed Pump. The wastewater is pumped from the refrigerated container using a variable-speed peristaltic pump drive equipped with a peristaltic pump head. Add the feed solution to the benchtop bioreactor through a fitting on the top flange. Determine the rate of feed addition to provide a retention time in the benchtop bioreactor that is numerically equivalent to the retention time in the target full-scale system. The wastewater shall be fed at a rate sufficient to achieve 90 to 100 percent of the target full-scale system residence time.

6.3.3 Treated wastewater feed. The benchtop bioreactor effluent exits at the bottom of the reactor through a tube and proceeds to the clarifier.

6.4 Clarifier. The effluent flows to a separate closed clarifier that allows separation of biomass and effluent (e.g., 2-liter pear-shaped glass separatory funnel, modified by removing the stopcock and adding a 25-mm OD glass tube at the bottom). Benchtop bioreactor effluent enters the clarifier through a tube inserted to a depth of 0.08 m (3 in.)

through a stopper at the top of the clarifier. System effluent flows from a tube inserted through the stopper at the top of the clarifier to a drain (or sample bottle when sampling). The underflow from the clarifier leaves from the glass tube at the bottom of the clarifier. Flexible tubing connects this fitting to the sludge recycle pump. This pump is coupled to a variable speed pump drive. The discharge from this pump is returned through a tube inserted in a port on the side of the benchtop bioreactor. An additional port is provided near the bottom of the benchtop bioreactor for sampling the reactor contents. The mixed liquor from the benchtop bioreactor flows into the center of the clarifier. The clarified system effluent separates from the biomass and flows through an exit near the top of the clarifier. There shall be no headspace in the clarifier.

6.5 Temperature Control Apparatus. Capable of maintaining the system at a temperature equal to the temperature of the full-scale system. The average temperature should be maintained within $\pm 2^\circ\text{C}$ of the set point.

6.5.1 Temperature Monitoring Device. A resistance type temperature probe or a thermocouple connected to a temperature readout with a resolution of 0.1°C or better.

6.5.2 Benchtop Bioreactor Heater. The heater is connected to the temperature control device.

6.6 Oxygen Control System. Maintain the dissolved oxygen concentration at the levels present in the full-scale system. Target full-scale activated sludge systems with dissolved oxygen concentration below 2 mg/L are required to maintain the dissolved oxygen concentration in the benchtop bioreactor within 0.5 mg/L of the target dissolved oxygen level. Target full-scale activated sludge systems with dissolved oxygen concentration above 2 mg/L are required to maintain the dissolved oxygen concentration in the benchtop bioreactor within 1.5 mg/L of the target dissolved oxygen concentration; however, for target full-scale activated sludge systems with dissolved oxygen concentrations above 2 mg/L, the dissolved oxygen concentration in the benchtop bioreactor may not drop below 1.5 mg/L. If the benchtop bioreactor is

outside the control range, the dissolved oxygen is noted and the reactor operation is adjusted.

6.6.1 Dissolved Oxygen Monitor. Dissolved oxygen is monitored with a polarographic probe (gas permeable membrane) connected to a dissolved oxygen meter (e.g., 0 to 15 mg/L, 0 to 50°C).

6.6.2 Benchtop Bioreactor Pressure Monitor. The benchtop bioreactor pressure is monitored through a port in the top flange of the reactor. This is connected to a gauge control with a span of 13-cm water vacuum to 13-cm water pressure or better. A relay is activated when the vacuum exceeds an adjustable setpoint which opens a solenoid valve (normally closed), admitting oxygen to the system. The vacuum setpoint controlling oxygen addition to the system shall be set at approximately 2.5 ± 0.5 cm water and maintained at this setting except during brief periods when the dissolved oxygen concentration is adjusted.

6.7 Connecting Tubing. All connecting tubing shall be Teflon or equivalent in impermeability. The only exception to this specification is the tubing directly inside the pump head of the wastewater feed pump, which may be Viton, Silicone or another type of flexible tubing.

Note: Mention of trade names or products does not constitute endorsement by the U.S. Environmental Protection Agency.

7.0. Reagents and Standards

7.1 Wastewater. Obtain a representative sample of wastewater at the inlet to the full-scale treatment plant if there is an existing full-scale treatment plant (See Section 6.3). If there is no existing full-scale treatment plant, obtain the wastewater sample as close to the point of determination as possible. Collect the sample by pumping the wastewater into the 20-L collapsible container. The loss of volatiles shall be minimized from the wastewater by collapsing the container before filling, by minimizing the time of filling, and by avoiding a headspace in the container after filling. If the wastewater requires the addition of nutrients to support the biomass growth and maintain biomass characteristics, those nutrients are

added and mixed with the container contents after the container is filled.

7.2 Biomass. Obtain the biomass or activated sludge used for rate constant determination in the bench-scale process from the existing full-scale process or from a representative biomass culture (e.g., biomass that has been developed for a future full-scale process). This biomass is preferentially obtained from a thickened acclimated mixed liquor sample. Collect the sample either by bailing from the mixed liquor in the aeration tank with a weighted container, or by collecting aeration tank effluent at the effluent overflow weir. Transport the sample to the laboratory within no more than 4 hours of collection. Maintain the biomass concentration in the benchtop bioreactor at the level of the target full-scale system ± 10 percent throughout the sampling period of the test method.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Benchtop Bioreactor Operation. Charge the mixed liquor to the benchtop bioreactor, minimizing headspace over the liquid surface to minimize entrainment of mixed liquor in the circulating gas. Fasten the benchtop bioreactor headplate to the reactor over the liquid surface. Maintain the temperature of the contents of the benchtop bioreactor system at the temperature of the target full-scale system, $\pm 2^\circ\text{C}$, throughout the testing period. Monitor and record the temperature of the reactor contents at least to the nearest 0.1°C .

8.1.1 Wastewater Storage. Collect the wastewater sample in the 20-L collapsible container. Store the container at 4°C throughout the testing period. Connect the container to the benchtop bioreactor feed pump.

8.1.2 Wastewater Flow Rate.

8.1.2.1 The hydraulic residence time of the aeration tank is calculated as the ratio of the volume of the tank (L) to the flow rate (L/min). At the beginning of a test, the container shall be connected to the feed pump and solution shall be pumped to the benchtop bioreactor at the required flow rate to achieve the calculated hydraulic residence time of wastewater in the aeration tank.

$$Q_{\text{test}} = Q_{\text{fs}} \frac{L}{V_{\text{fs}}} \quad \text{Eq. 304B-1}$$

Where:

Q_{test} = wastewater flow rate (L/min)

Q_{fs} = average flow rate of full-scale process (L/min)

V_{fs} = volume of full-scale aeration tank (L)

8.1.2.2 The target flow rate in the test apparatus is the same as the flow rate in the target full-scale process multiplied by the ratio of benchtop bioreactor volume (*e.g.*, 6 L) to the volume of the full-scale aeration tank. The hydraulic residence time shall be maintained at 90 to 100 percent of the residence time maintained in the target full-scale unit. A nominal flow rate is set on the pump based on a pump calibration. Changes in the elasticity of the tubing in the pump head and the accumulation of material in the tubing affect this calibration. The nominal pumping rate shall be changed as necessary based on volumetric flow measurements. Discharge the benchtop bioreactor effluent to a wastewater storage, treatment, or disposal facility, except during sampling or flow measurement periods.

8.1.3 Sludge Recycle Rate. Set the sludge recycle rate at a rate sufficient to prevent accumulation in the bottom of the clarifier. Set the air circulation rate sufficient to maintain the biomass in suspension.

8.1.4 Benchtop Bioreactor Operation and Maintenance. Temperature, dissolved oxygen concentration, flow rate, and air circulation rate shall be measured and recorded three times throughout each day of testing. If other parameters (such as pH) are measured and maintained in the target full-scale unit, these parameters shall, where appropriate, be monitored and maintained to full-scale specifications in the benchtop bioreactor. At the beginning of each sampling period (section 8.2), sample the benchtop bioreactor contents for suspended solids analysis. Take this sample by loosening a clamp on a length of tubing attached to the lower side port. Determine the suspended solids gravimetrically by the Gooch crucible/glass fiber filter method for total suspended solids, in accordance with Standard Methods³ or equivalent. When necessary, sludge shall be wasted from the lower side port of the benchtop bioreactor, and the volume that is wasted shall be replaced with an equal volume of the benchtop bioreactor effluent. Add thickened activated sludge mixed liquor as necessary to the benchtop bioreactor to increase the suspended solids concentration to the desired level. Pump

this mixed liquor to the benchtop bioreactor through the upper side port (Item 24 in Figure 304B-1). Change the membrane on the dissolved oxygen probe before starting the test. Calibrate the oxygen probe immediately before the start of the test and each time the membrane is changed. The scrubber solution shall be replaced each weekday with 175 mL 45 percent W/W KOH solution to which five drops of 0.2 percent alizarin yellow indicator in water have been added. The potassium hydroxide solution in the alkaline scrubber shall be changed if the alizarin yellow dye color changes.

8.1.5 Inspection and Correction Procedures. If the feed line tubing becomes clogged, replace with new tubing. If the feed flow rate is not within 5 percent of target flow any time the flow rate is measured, reset pump or check the flow measuring device and measure flow rate again until target flow rate is achieved.

8.2 Test Sampling. At least two and one half hydraulic residence times after the system has reached the targeted specifications shall be permitted to elapse before the first sample is taken. Effluent samples of the clarifier discharge (Item 20 in Figure 304B-1) and the influent wastewater feed are collected in 40-mL septum vials to which two drops of 1:10 hydrochloric acid (HCl) in water have been added. Sample the clarifier discharge directly from the drain line. These samples will be composed of the entire flow from the system for a period of several minutes. Feed samples shall be taken from the feed pump suction line after temporarily stopping the benchtop bioreactor feed, removing a connector, and squeezing the collapsible feed container. Store both influent and effluent samples at 4°C immediately after collection and analyze within 8 hours of collection.

8.2.1 Frequency of Sampling. During the test, sample and analyze the wastewater feed and the clarifier effluent at least six times. The sampling intervals shall be separated by at least 8 hours. During any individual sampling interval, sample the wastewater feed simultaneously with or immediately after the effluent sample. Calculate the RSD of the amount removed (*i.e.*, effluent concentration—wastewater feed concentration). The

RSD values shall be <15 percent. If an RSD value is >15 percent, continue sampling and analyzing influent and effluent sets of samples until the RSD values are within specifications.

8.2.2 Sampling After Exposure of System to Atmosphere. If, after starting sampling procedures, the benchtop bioreactor system is exposed to the atmosphere (due to leaks, maintenance, etc.), allow at least one hydraulic residence time to elapse before resuming sampling.

9.0 Quality Control

9.1 Dissolved Oxygen. Fluctuation in dissolved oxygen concentration may occur for numerous reasons, including undetected gas leaks, increases and decreases in mixed liquor suspended solids resulting from cell growth and solids loss in the effluent stream, changes in diffuser performance, cycling of effluent flow rate, and overcorrection due to faulty or sluggish dissolved oxygen probe response. Control the dissolved oxygen concentration in the benchtop bioreactor by changing the proportion of oxygen in the circulating aeration gas. Should the dissolved oxygen concentration drift below the designated experimental condition, bleed a small amount of aeration gas from the system on the pressure side (*i.e.*, immediately upstream of one of the diffusers). This will create a vacuum in the system, triggering the pressure sensitive relay to open the solenoid valve and admit oxygen to the system. Should the dissolved oxygen concentration drift above the designated experimental condition, slow or stop the oxygen input to the system until the dissolved oxygen concentration approaches the correct level.

9.2 Sludge Wasting.

9.2.1 Determine the suspended solids concentration (section 8.1.4) at the beginning of a test, and once per day thereafter during the test. If the test is completed within a two day period, determine the suspended solids concentration after the final sample set is taken. If the suspended solids concentration exceeds the specified concentration, remove a fraction of the sludge from the benchtop bioreactor. The required volume of mixed liquor to remove is determined as follows:

$$V_w = V_r \left(\frac{S_m - S_s}{S_m} \right) \quad \text{Eq. 304B-2}$$

Where:

V_w is the wasted volume (Liters),

V_r is the volume of the benchtop bioreactor (Liters),

S_m is the measured solids (g/L), and

S_s is the specified solids (g/L).

9.2.2 Remove the mixed liquor from the benchtop bioreactor by loosening a

clamp on the mixed liquor sampling tube and allowing the required volume to drain to a graduated flask. Clamp the tube when the correct volume has been wasted. Replace the volume of the liquid wasted by pouring the same volume of effluent back into the

benchtop bioreactor. Dispose of the waste sludge properly.

9.3 Sludge Makeup. In the event that the suspended solids concentration is lower than the specifications, add makeup sludge back into the benchtop bioreactor. Determine the amount of sludge added by the following equation:

$$V_w = V_r \left(\frac{S_s - S_m}{S_w} \right) \quad \text{Eq. 304B-3}$$

Where:

V_w is the volume of sludge to add (Liters),

V_r is the volume of the benchtop bioreactor (Liters),

S_w is the solids in the makeup sludge (g/L),

S_m is the measured solids (g/L), and

S_s is the specified solids (g/L).

10.0 Calibration and Standardizations

10.1 Wastewater Pump Calibration. Determine the wastewater flow rate by collecting the system effluent for a time period of at least one hour, and measuring the volume with a graduated cylinder. Record the collection time period and volume collected. Determine flow rate. Adjust the pump speed to deliver the specified flow rate.

10.2 Calibration Standards. Prepare calibration standards from pure certified standards in an aqueous medium. Prepare and analyze three concentrations of calibration standards for each target component (or for a mixture of components) in triplicate daily throughout the analyses of the test samples. At each concentration level, a single calibration shall be within 5 percent of the average of the three calibration results. The low and medium calibration standards shall bracket the expected concentration of

the effluent (treated) wastewater. The medium and high standards shall bracket the expected influent concentration.

11.0 Analytical Test Procedures

11.1 Analysis. If the identity of the compounds of interest in the wastewater is not known, a representative sample of the wastewater shall be analyzed in order to identify all of the compounds of interest present. A gas chromatography/mass spectrometry screening method is recommended.

11.1.1 After identifying the compounds of interest in the wastewater, develop and/or use one or more analytical technique capable of measuring each of those compounds (more than one analytical technique may be required, depending on the characteristics of the wastewater). Method 18, found in appendix A of 40 CFR 60, may be used as a guideline in developing the analytical technique. Purge and trap techniques may be used for analysis providing the target components are sufficiently volatile to make this technique appropriate. The limit of quantitation for each compound shall be determined.¹ If the effluent concentration of any target compound is below the limit of quantitation determined for that compound, the operation of the Method 304 unit may

be altered to attempt to increase the effluent concentration above the limit of quantitation. Modifications to the method shall be approved prior to the test. The request should be addressed to Method 304 contact, Emissions Measurement Center, Mail Drop 19, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711.

12.0 Data Analysis and Calculations

12.1 Nomenclature. The following symbols are used in the calculations.

C_i = Average inlet feed concentration for a compound of interest, as analyzed (mg/L)

C_o = Average outlet (effluent) concentration for a compound of interest, as analyzed (mg/L)

X = Biomass concentration, mixed liquor suspended solids (g/L)

t = Hydraulic residence time in the benchtop bioreactor (hours)

V = Volume of the benchtop bioreactor (L)

Q = Flow rate of wastewater into the benchtop bioreactor, average (L/hour)

12.2 Residence Time. The hydraulic residence time of the benchtop bioreactor is equal to the ratio of the volume of the benchtop bioreactor (L) to the flow rate (L/h)

$$t = \frac{V}{Q} \quad \text{Eq. 304B-4}$$

12.3 Rate of Biodegradation. Calculate the rate of biodegradation for

each component with the following equation:

$$\text{Rate} \left(\frac{\text{mg}}{\text{L} - \text{h}} \right) = \frac{C_i - C_o}{t} \quad \text{Eq. 304B-5}$$

12.4 First-Order Biorate Constant. Calculate the first-order biorate constant

(K1) for each component with the following equation:

$$Kl \left(\frac{L}{g-h} \right) = \frac{C_i - C_o}{t C_o X} \quad \text{Eq. 304B-6}$$

12.5 Relative Standard Deviation (RSD). Determine the standard deviation of both the influent and effluent sample

concentrations (S) using the following equation:

$$RSD = \frac{100}{\bar{S}} \left(\sum_{i=1}^n \frac{(S_i - \bar{S})^2}{(n-1)} \right)^{1/2} \quad \text{Eq. 304B-7}$$

12.6 Determination of Percent Air Emissions and Percent Biodegraded. Use the results from this test method and follow the applicable procedures in appendix C of 40 CFR Part 63, entitled, "Determination of the Fraction Biodegraded (F_{bio}) in a Biological Treatment Unit" to determine F_{bio} .

13.0 *Method Performance. [Reserved]*

14.0 *Pollution Prevention. [Reserved]*

15.0 *Waste Management. [Reserved]*

16.0 *References*

1. "Guidelines for data acquisition and data quality evaluation in Environmental Chemistry", Daniel MacDoughal, Analytical Chemistry, Volume 52, p. 2242, 1980.

2. Test Method 18, 40 CFR 60, Appendix A.

3. Standard Methods for the Examination of Water and Wastewater, 16th Edition,

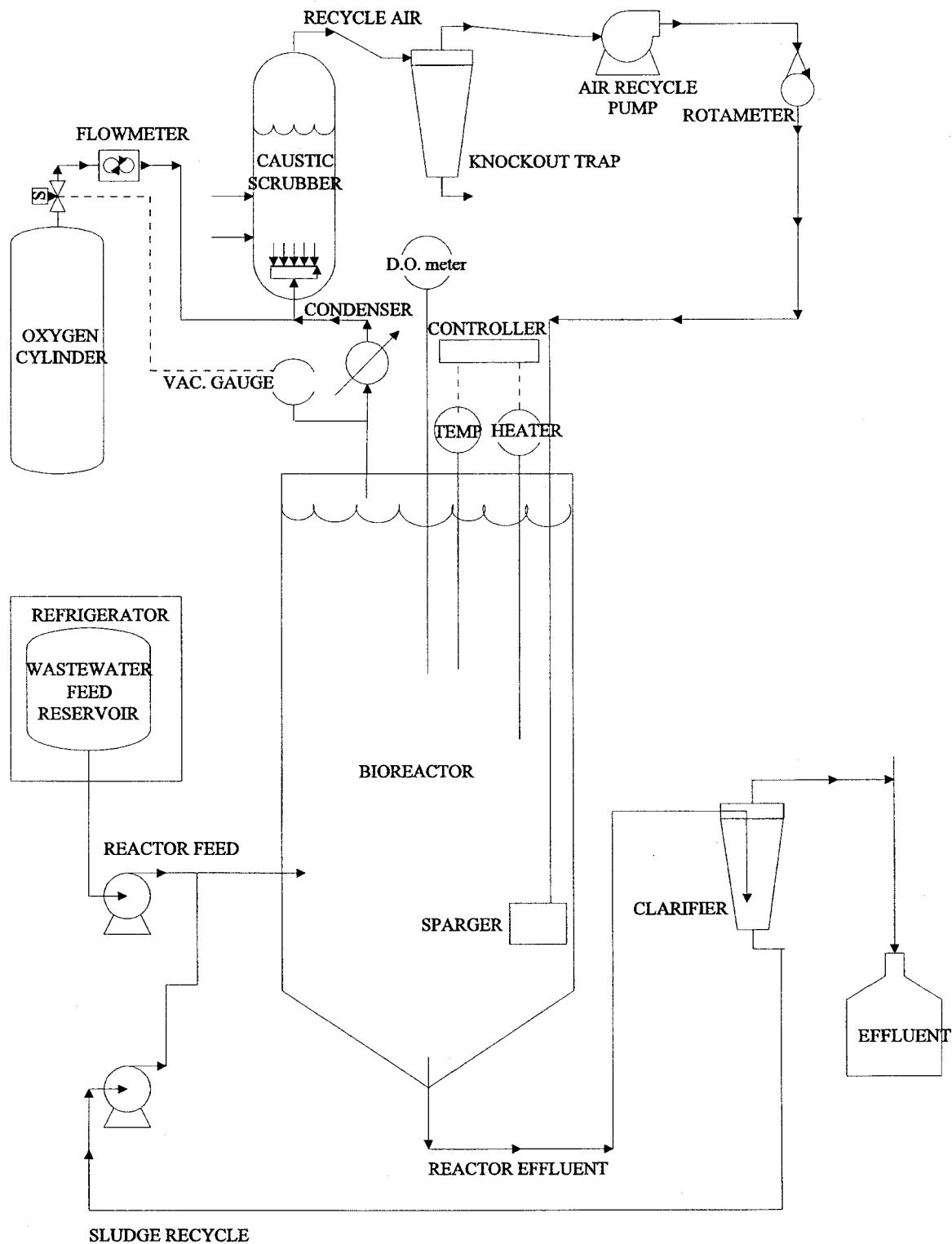
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4. Water—7, Hazardous Waste Treatment, Storage, and Disposal Facilities (TSDF)—Air Emission Models, U.S. Environmental Protection Agency, EPA-450/3-87-026, Review Draft, November 1989.

5. Chemdat7, Hazardous Waste Treatment, Storage, and Disposal Facilities (TSDF)—Air Emission Models, U.S. Environmental Protection Agency, EPA-450/3-87-026, Review Draft, November 1989.

BILLING CODE 6560-50-P

17.0 Tables, Diagrams, Flowcharts, and Validation Data



EPA METHOD 304B BIOREACTOR SYSTEM

Method 305: Measurement of Emission Potential of Individual Volatile Organic Compounds in Waste

Note: This method does not include all of the specifications (e.g., equipment and supplies) and procedures (e.g., sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in 40 CFR Part 60, Appendix A. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least Method 25D.

1.0 Scope and Application

1.1 Analyte. Volatile Organics. No CAS No. assigned.

1.2 Applicability. This procedure is used to determine the emission potential of individual volatile organics (VOs) in waste.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 The heated purge conditions established by Method 25D (40 CFR Part 60, Appendix A) are used to remove VOs from a 10 gram sample of waste suspended in a 50/50 solution of polyethylene glycol (PEG) and water. The purged VOs are quantified by using the sample collection and analytical techniques (e.g. gas chromatography) appropriate for the VOs present in the waste. The recovery efficiency of the sample collection and analytical technique is determined for each waste matrix. A correction factor is determined for each compound (if acceptable recovery criteria requirements are met of 70 to 130 percent recovery for every target compound), and the measured waste concentration is corrected with the correction factor for each compound. A minimum of three replicate waste samples shall be analyzed.

3.0 Definitions [Reserved]

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

6.0 Equipment and Supplies

6.1 Method 25D Purge Apparatus.

6.1.1 Purge Chamber. The purge chamber shall accommodate the 10 gram sample of waste suspended in a matrix of 50 mL of PEG and 50 mL of deionized, hydrocarbon-free water. Three fittings are used on the glass chamber top. Two #7 Ace-threads are used for the purge gas inlet and outlet connections. A #50 Ace-thread is used to connect the top of the chamber to the base (see Figure 305-1). The base of the chamber has a side-arm equipped with a #22 Sovirel fitting to allow for easy sample introductions into the chamber. The dimensions of the chamber are shown in Figure 305-1.

6.1.2 Flow Distribution Device (FDD). The FDD enhances the gas-to-liquid contact for improved purging efficiency. The FDD is a 6 mm OD (0.2 in) by 30 cm (12 in) long glass tube equipped with four arm bubblers as shown in Figure 305-1. Each arm shall have an opening of 1 mm (0.04 in) in diameter.

6.1.3 Coalescing Filter. The coalescing filter serves to discourage aerosol formation of sample gas once it leaves the purge chamber. The glass filter has a fritted disc mounted 10 cm (3.9 in) from the bottom. Two #7 Ace-threads are used for the inlet and outlet connections. The dimensions of the chamber are shown in Figure 305-2.

6.1.4 Oven. A forced convection airflow oven capable of maintaining the purge chamber and coalescing filter at $75 \pm 2^\circ\text{C}$ ($167 \pm 3.6^\circ\text{F}$).

6.1.5 Toggle Valve. An on/off valve constructed from brass or stainless steel rated to 100 psig. This valve is placed in line between the purge nitrogen source and the flow controller.

6.1.6 Flow Controller. High-quality stainless steel flow controller capable of restricting a flow of nitrogen to 6 ± 0.06 L/min (0.2 ± 0.002 ft³/min) at 40 psig.

6.1.7 Polyethylene Glycol Cleaning System.

6.1.7.1 Round-Bottom Flask. One liter, three-neck glass round-bottom flask for cleaning PEG. Standard taper 24/40 joints are mounted on each neck.

6.1.7.2 Heating Mantle. Capable of heating contents of the 1-L flask to 120°C (248°F).

6.1.7.3 Nitrogen Bubbler. Teflon® or glass tube, 0.25 in OD (6.35 mm).

6.1.7.4 Temperature Sensor. Partial immersion glass thermometer.

6.1.7.5 Hose Adapter. Glass with 24/40 standard tapered joint.

6.2 Volatile Organic Recovery System.

6.2.1 Splitter Valve (Optional). Stainless steel cross-pattern valve capable of splitting nominal flow rates from the purge flow of 6 L/min (0.2 ft³/min). The valve shall be maintained at

$75 \pm 2^\circ\text{C}$ ($167 \pm 3.6^\circ\text{F}$) in the heated zone and shall be placed downstream of the coalescing filter. It is recommended that 0.125 in OD (3.175 mm) tubing be used to direct the split vent flow from the heated zone. The back pressure caused by the 0.125 in OD (3.175 mm) tubing is critical for maintaining proper split valve operation.

Note: The splitter valve design is optional; it may be used in cases where the concentration of a pollutant would saturate the adsorbents.

6.2.2 Injection Port. Stainless steel 1/4 in OD (6.35 mm) compression fitting tee with a 6 mm (0.2 in) septum fixed on the top port. The injection port is the point of entry for the recovery study solution. If using a gaseous standard to determine recovery efficiency, connect the gaseous standard to the injection port of the tee.

6.2.3 Knockout Trap (Optional but Recommended). A 25 mL capacity glass reservoir body with a full-stem impinger (to avoid leaks, a modified midget glass impinger with a screw cap and ball/socket clamps on the inlet and outlet is recommended). The empty impinger is placed in an ice water bath between the injection port and the sorbent cartridge. Its purpose is to reduce the water content of the purge gas (saturated at 75°C (167°F)) before the sorbent cartridge.

6.2.4 Insulated Ice Bath. A 350 mL dewar or other type of insulated bath is used to maintain ice water around the knockout trap.

6.2.5 Sorbent Cartridges. Commercially available glass or stainless steel cartridge packed with one or more appropriate sorbents. The amount of adsorbent packed in the cartridge depends on the breakthrough volume of the test compounds but is limited by back pressure caused by the packing (not to exceed 7 psig). More than one sorbent cartridge placed in series may be necessary depending upon the mixture of the measured components.

6.2.6 Volumetric Glassware. Type A glass 10 mL volumetric flasks for measuring a final volume from the water catch in the knockout trap.

6.2.7 Thermal Desorption Unit. A clam-shell type oven, used for the desorption of direct thermal desorption sorbent tubes. The oven shall be capable of increasing the temperature of the desorption tubes rapidly to recommended desorption temperature.

6.2.8 Ultrasonic Bath. Small bath used to agitate sorbent material and desorption solvent. Ice water shall be used in the bath because of heat transfer caused by operation of the bath.

6.2.9 Desorption Vials. Four-dram (15 mL) capacity borosilicate glass vials with Teflon-lined caps.

6.3 Analytical System. A gas chromatograph (GC) is commonly used to separate and quantify compounds from the sample collection and recovery procedure. Method 18 (40 CFR Part 60, Appendix A) may be used as a guideline for determining the appropriate GC column and GC detector based on the test compounds to be determined. Other types of analytical instrumentation may be used (HPLC) in lieu of GC systems as long as the recovery efficiency criteria of this method are met.

6.3.1 Gas Chromatograph (GC). The GC shall be equipped with a constant-temperature liquid injection port or a heated sampling loop/valve system, as appropriate. The GC oven shall be temperature-programmable over the useful range of the GC column. The choice of detectors is based on the test compounds to be determined.

6.3.2 GC Column. Select the appropriate GC column based on (1) literature review or previous experience, (2) polarity of the analytes, (3) capacity of the column, or (4) resolving power (e.g., length, diameter, film thickness) required.

6.3.3 Data System. A programmable electronic integrator for recording, analyzing, and storing the signal generated by the detector.

7.0 Reagents and Standards

7.1 Method 25D Purge Apparatus.

7.1.1 Polyethylene Glycol (PEG). Ninety-eight percent pure organic polymer with an average molecular weight of 400 g/mol. Volatile organics are removed from the PEG prior to use by heating to $120 \pm 5^\circ\text{C}$ ($248 \pm 9^\circ\text{F}$) and purging with pure nitrogen at 1 L/min ($0.04 \text{ ft}^3/\text{min}$) for 2 hours. After purging and heating, the PEG is maintained at room temperature under a nitrogen purge maintained at 1 L/min ($0.04 \text{ ft}^3/\text{min}$) until used. A typical apparatus used to clean the PEG is shown in Figure 305-3.

7.1.2 Water. Organic-free deionized water is required.

7.1.3 Nitrogen. High-purity nitrogen (less than 0.5 ppm total hydrocarbons) is used to remove test compounds from the purge matrix. The source of nitrogen shall be regulated continuously to 40 psig before the on/off toggle valve.

7.2 Volatile Organic Recovery System.

7.2.1 Water. Organic-free deionized water is required.

7.2.2 Desorption Solvent (when used). Appropriate high-purity (99.99 percent) solvent for desorption shall be used. Analysis shall be performed (utilizing the same analytical technique as that used in the analysis of the waste samples) on each lot to determine purity.

7.3 Analytical System. The gases required for GC operation shall be of the highest obtainable purity (hydrocarbon free). Consult the operating manual for recommended settings.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Assemble the glassware and associated fittings (see Figures 305-3 and 305-4, as appropriate) and leak-check the system (approximately 7 psig is the target pressure). After an initial leak check, mark the pressure gauge and use the initial checkpoint to monitor for leaks throughout subsequent analyses. If the pressure in the system drops below the target pressure at any time during analysis, that analysis shall be considered invalid.

8.2 Recovery Efficiency Determination. Determine the individual recovery efficiency (RE) for each of the target compounds in duplicate before the waste samples are analyzed. To determine the RE, generate a water blank (Section 11.1) and use the injection port to introduce a known volume of spike solution (or certified gaseous standard) containing all of the target compounds at the levels expected in the waste sample. Introduce the spike solution immediately after the nitrogen purge has been started (Section 8.3.2). Follow the procedures outlined in Section 8.3.3. Analyze the recovery efficiency samples using the techniques described in Section 11.2. Determine the recovery efficiency (Equation 305-1, Section 12.2) by comparing the amount of compound recovered to the theoretical amount spiked. Determine the RE twice for each compound; the relative standard deviation, (RSD) shall be ≤ 10 percent for each compound. If the RSD for any compound is not ≤ 10 percent, modify the sampling/analytical procedure and complete an RE study in duplicate, or continue determining RE until the RSD meets the acceptable criteria. The average RE shall be $0.70 \leq \text{RE} \leq 1.30$ for each compound. If the average RE does not meet these criteria, an alternative sample collection and/or

analysis technique shall be developed and the recovery efficiency determination shall be repeated for that compound until the criteria are met for every target compound. Example modifications of the sampling/analytical system include changing the adsorbent material, changing the desorption solvent, utilizing direct thermal desorption of test compounds from the sorbent tubes, utilizing another analytical technique.

8.3 Sample Collection and Recovery.

8.3.1 The sample collection procedure in Method 25D shall be used to collect (into a preweighed vial) 10 g of waste into PEG, cool, and ship to the laboratory. Remove the sample container from the cooler and wipe the exterior to remove any ice or water. Weigh the container and sample to the nearest 0.01 g and record the weight. Pour the sample from the container into the purge flask. Rinse the sample container three times with approximately 6 mL of PEG (or the volume needed to total 50 mL of PEG in the purge flask), transferring the rinses to the purge flask. Add 50 mL of organic-free deionized water to the purge flask. Cap the purge flask tightly in between each rinse and after adding all the components into the flask.

8.3.2 Allow the oven to equilibrate to $75 \pm 2^\circ\text{C}$ ($167 \pm 3.6^\circ\text{F}$). Begin the sample recovery process by turning the toggle valve on, thus allowing a 6 L/min flow of pure nitrogen through the purge chamber.

8.3.3 Stop the purge after 30 min. Immediately remove the sorbent tube(s) from the apparatus and cap both ends. Remove the knockout trap and transfer the water catch to a 10 mL volumetric flask. Rinse the trap with organic-free deionized water and transfer the rinse to the volumetric flask. Dilute to the 10 mL mark with water. Transfer the water sample to a sample vial and store at 4°C (39.2°F) with zero headspace. The analysis of the contents of the water knockout trap is optional for this method. If the target compounds are water soluble, analysis of the water is recommended; meeting the recovery efficiency criteria in these cases would be difficult without adding the amount captured in the knockout trap.

9.0 Quality Control

9.1 Miscellaneous Quality Control Measures.

Section	Quality control measure	Effect
8.1	Sampling equipment leak-check	Ensures accurate measurement of sample volume.
8.2	Recovery efficiency (RE) determination for each measured compound..	Ensures accurate sample collection and analysis.
8.3	Calibration of analytical instrument with at least 3 calibration standards..	Ensures linear measurement of compounds over the instrument span.

10.0 Calibration and Standardization

10.1 The analytical instrument shall be calibrated with a minimum of three levels of standards for each compound whose concentrations bracket the concentration of test compounds from the sorbent tubes. Liquid calibration standards shall be used for calibration in the analysis of the solvent extracts. The liquid calibration standards shall be prepared in the desorption solvent matrix. The calibration standards may be prepared and injected individually or as a mixture. If thermal desorption and focusing (onto another sorbent or cryogen focusing) are used, a certified gaseous mixture or a series of gaseous standards shall be used for calibration of the instrument. The gaseous standards shall be focused and analyzed in the same manner as the samples.

10.2 The analytical system shall be certified free from contaminants before a calibration is performed (see Section 11.1). The calibration standards are used to determine the linearity of the analytical system. Perform an initial calibration and linearity check by analyzing the three calibration standards for each target compound in triplicate starting with the lowest level and continuing to the highest level. If the triplicate analyses do not agree within 5 percent of their average, additional analyses will be needed until the 5 percent criteria is met. Calculate the response factor (Equation 305-3, Section 12.4) from the average area counts of the injections for each concentration level. Average the response factors of the standards for each compound. The linearity of the detector is acceptable if the response factor of each compound at a particular concentration is within 10 percent of the overall mean response factor for that compound. Analyze daily a mid-level calibration standard in duplicate and calculate a new response factor. Compare the daily response factor average to the average response factor calculated for the mid-level calibration during the initial linearity check; repeat the three-level calibration procedure if the daily average response factor differs from the initial linearity check mid-level response factor by more than 10 percent. Otherwise, proceed with the sample analysis.

11.0 Analytical Procedure

11.1 Water Blank Analysis. A water blank shall be analyzed daily to determine the cleanliness of the purge and recovery system. A water blank is generated by adding 60 mL of organic-free deionized water to 50 mL of PEG in the purge chamber. Treat the blank as described in Sections 8.3.2 and 8.3.3. The purpose of the water blank is to insure that no contaminants exist in the sampling and analytical apparatus which would interfere with the quantitation of the target compounds. If contaminants are present, locate the source of contamination, remove it, and repeat the water blank analysis.

11.2 Sample Analysis. Sample analysis in the context of this method refers to techniques to remove the target compounds from the sorbent tubes, separate them using a chromatography technique, and quantify them with an appropriate detector. Two types of sample extraction techniques typically used for sorbents include solvent desorption or direct thermal desorption of test compounds to a secondary focusing unit (either sorbent or cryogen based). The test compounds are then typically transferred to a GC system for analysis. Other analytical systems may be used (e.g., HPLC) in lieu of GC systems as long as the recovery efficiency criteria of this method are met.

11.2.1 Recover the test compounds from the sorbent tubes that require solvent desorption by transferring the adsorbent material to a sample vial containing the desorption solvent. The desorption solvent shall be the same as the solvent used to prepare calibration standards. The volume of solvent depends on the amount of adsorbed material to be desorbed (1.0 mL per 100 mg of adsorbent material) and also on the amount of test compounds present. Final volume adjustment and or dilution can be made so that the concentration of test compounds in the desorption solvent is bracketed by the concentration of the calibration solutions. Ultrasonicate the desorption solvent for 15 min in an ice bath. Allow the sample to sit for a period of time so that the adsorbent material can settle to the bottom of the vial. Transfer the solvent with a pasteur pipet (minimizing the amount of adsorbent

material taken) to another vial and store at 4 °C (39.2 °F).

11.2.2 Analyze the desorption solvent or direct thermal desorption tubes from each sample using the same analytical parameters used for the calibration standard. Calculate the total weight detected for each compound (Equation 305-4, Section 12.5). The slope (area/amount) and y-intercept are calculated from the line bracketed between the two closest calibration points. Correct the concentration of each waste sample with the appropriate recovery efficiency factor and the split flow ratio (if used). The final concentration of each individual test compound is calculated by dividing the corrected measured weight for that compound by the weight of the original sample determined in Section 8.3.1 (Equation 305-5, Section 12.6).

11.2.3 Repeat the analysis for the three samples collected in Section 8.3. Report the corrected concentration of each of the waste samples, average waste concentration, and relative standard deviation (Equation 305-6, Section 12.7).

12.0 Data Analysis and Calculations.

12.1 Nomenclature.

A_S = Mean area counts of test compound in standard.

A_U = Mean area counts of test compound in sample desorption solvent.

b = Y-intercept of the line formed between the two closest calibration standards that bracket the concentration of the sample.

C_T = Amount of test compound (μg) in calibration standard.

C_F = Correction for adjusting final amount of sample detected for losses during individual sample runs.

F_P = Nitrogen flow through the purge chamber (6 L/min).

F_S = Nitrogen split flow directed to the sample recovery system (use 6 L/min if split flow design was not used).

PPM = Final concentration of test compound in waste sample [$\mu\text{g/g}$ (which is equivalent to parts per million by weight (ppmw))].

RE = Recovery efficiency for adjusting final amount of sample detected for losses due to inefficient trapping and desorption techniques.

R.F. = Response factor for test compound, calculated from a calibration standard.

S = Slope of the line (area counts/ C_T) formed between two closest calibration points that bracket the concentration of the sample.

W_C = Weight of test compound expected to be recovered in spike solution based on theoretical amount (μg).

W_E = Weight of vial and PEG (g).

W_F = Weight of vial, PEG and waste sample (g).

W_S = Weight of original waste sample (g).

W_T = Corrected weight of test compound measured (μg) in sample.

W_X = Weight of test compound measured during analysis of

recovery efficiency spike samples (μg).

12.2 Recovery efficiency for determining trapping/desorption efficiency of individual test compounds in the spike solution, decimal value.

$$\text{RE} = \frac{W_X}{W_C} \quad \text{Eq. 305-1}$$

12.3 Weight of waste sample (g).

$$W_S = W_F - W_E \quad \text{Eq. 305-2}$$

12.4 Response factor for individual test compounds.

$$\text{RF} = \frac{C_T}{A_S} \quad \text{Eq. 305-3}$$

12.5 Corrected weight of a test compound in the sample, in μg .

$$W_T = \frac{A_u - b}{S} \times \frac{1}{\text{RE}} \times \frac{F_p}{F_s} \quad \text{Eq. 305-4}$$

12.6 Final concentration of a test compound in the sample in ppmw.

$$\text{PPM} = \frac{W_T}{W_S} \quad \text{Eq. 305-5}$$

12.7 Relative standard deviation (RSD) calculation.

$$\text{RSD} = \frac{100}{\overline{\text{PPM}}} \sqrt{\frac{\sum_{i=1}^n (\text{PPM}_i - \overline{\text{PPM}})^2}{n-1}} \quad \text{Eq. 305-6}$$

13.0 Method Performance. [Reserved]

14.0 Pollution Prevention. [Reserved]

15.0 Waste Management. [Reserved]

16.0 References. [Reserved]